



# Technical Note

67

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## ON THE NATURE OF THE CRYSTAL FIELD APPROXIMATION



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U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

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# NATIONAL BUREAU OF STANDARDS

## *Technical Note*

67

OCTOBER 1960

### ON THE NATURE OF THE CRYSTAL FIELD APPROXIMATION

Henry Goldberg and Charles Herzfeld

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# ON THE NATURE OF THE CRYSTAL FIELD APPROXIMATION\*

Henry Goldberg<sup>+</sup> and C. M. Herzfeld

National Bureau of Standards

## ABSTRACT

A new method is developed for the treatment of molecular interactions, and is applied to a system consisting of a hydrogen atom in a 2p state and a hydrogen molecule in the ground state. The interaction of these two species is calculated using ordinary crystal field theory and also the new method. A comparison of the results shows some of the shortcomings of the conventional crystal field theory, and provides corrections to it. The new method consists of 1) expanding all electron terms of the total Hamiltonian for the system which involve interactions between the atom and the molecule, thus transforming the interaction Hamiltonian into sums of products of one-electron operators, and 2) of using properly antisymmetrized wave functions made up of products of atom and molecule eigenfunctions. The calculations show the effect of the neglect of overlap and exchange in ordinary crystal field theory.

All calculations and results are presented in full detail. Transformations of three-center to two-center integrals are given explicitly.

\*Based in part on a thesis submitted by Henry Goldberg to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics.

<sup>+</sup>Present address: University of Buffalo, Buffalo, New York.

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## I. INTRODUCTION

Apparently Freed and Spedding<sup>1</sup> were the first to point out that the electrostatic fields in ionic crystals would lift the degeneracy of states of ions in the crystal, and thus affect their magnetic and optical properties. Shortly thereafter Becquerel<sup>2</sup>, and Brunetti and Ollano<sup>3</sup> studied the effects of such crystal fields, and Bethe<sup>4</sup> gave an extended group theoretical discussion of the effects. A little later Van Vleck<sup>5</sup> and his students laid the foundations for the practical use of crystal field theory. The development of paramagnetic resonance and the revival of optical spectroscopy of solids after 1945 gave strong impetus to further developments of crystal field theory. These developments are summarized in several recent reviews<sup>6-9</sup>.

Crystal field theory has been extraordinarily useful in explaining and correlating a wide variety of magnetic, optical and chemical properties. Relatively little attention has been paid, however, to the basic validity or meaning of the method. In this paper we examine some of the fundamental properties of crystal field theory. In particular we examine some of the approximations implied by the theory.

Usually, crystal field theory proceeds as follows. The Hamiltonian of the species of interest<sup>10</sup> in the solid includes the terms appropriate for the free reference ion, together with some terms which express its interactions with the solid. These interactions are assumed to be

largely electrostatic, and are assumed to arise chiefly from the neighbors of the reference ion. The application of the theory has usually two parts:

1) A Hamiltonian for the perturbed reference ion is set up, using such information of the crystal structure as is available. The arrangement of neighboring ions or molecules determines the symmetry of the electrostatic field in which the reference ion finds itself. In the absence of definite structural information plausible assumptions about the geometry must be made. The matrix elements of this Hamiltonian contain parameters which give the (initially unknown) magnitudes of the interactions. The eigenvalues and eigenfunctions are calculated as a function of these parameters. The values of the parameters are adjusted to give the best agreement between predicted and observed properties. In this way the magnetic susceptibility, paramagnetic resonance absorption, optical spectrum, thermodynamic, and magneto-optical properties of the material can be accounted for. If adequate agreement can be obtained using fewer parameters than independent sets of data, the general assumptions about the nature of the ~~system~~ and the symmetry of the structure are probably correct.

2) One attempts to calculate the values of the parameters numerically using various detailed models, to see if a model can be found with numerical parameters equal to those obtained from the fit with

experiment. This problem is more difficult, and the results much less certain than those of part one. The reasons for attempting even crude numerical calculations of the parameters are these: Such calculations serve to check the reasonableness of the general model, and they may shed some light on the details of the structure of the center.

Attempts to calculate the parameters in crystal field theory from electrostatic models have had mixed success. A recent careful calculation by Kleiner<sup>11</sup> of the crystal field splitting constant in chrome alum,  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , gave the wrong magnitude and sign. Tanabe and Sugano<sup>12</sup> have carried out calculations of the crystal field parameter on the basis of a molecular orbital treatment of the complex made up of the reference ion and its nearest neighbors. They find a parameter of correct sign and magnitude. Their chief improvement over Kleiner's calculation is the careful treatment of exchange between the electrons on the reference ion and those on the nearest neighbors.

It is clear that it must be possible to give a theory of the perturbations of the reference ion in the crystal which is basically like crystal field theory. The Wigner-Eckart theorem guarantees that such a theory will have a finite number of scalar parameters if a finite number of electron configurations of the reference ion are sufficient to describe its properties<sup>9</sup>. It would, however, be interesting to see the exact nature of the crystal field approximation by comparing it with a theory which is both relatively clear and successful, such as molecular orbital theory. In this paper we carry out such a comparison between crystal field theory and MO theory,

and are able to make explicit the nature of the crystal field approximation. The basic approach is, in some ways, similar to Moffitt's method of atoms in molecules<sup>13</sup>. To make the problem as simple as possible, we study the case of an H atom perturbed by an H<sub>2</sub> molecule. Systems of this type have been studied successfully with crystal field methods: N atoms perturbed by N<sub>2</sub> molecules have been treated by Herzfeld<sup>14</sup>, and O atoms perturbed by N<sub>2</sub> molecules by Goldberg and Herzfeld<sup>15</sup>. The hydrogen system exhibits all the features needed for an application of crystal field theory: The H atom is taken in a 2p state, which has orbital degeneracy, and the H<sub>2</sub> molecule has an electric quadrupole moment whose field lifts the orbital degeneracy of the atom. Furthermore, this system gives rise to a three-electron problem, which can be treated with molecular orbital techniques without exorbitant complications.

The following procedure is used: The total Hamiltonian for the three electrons and three nuclei is written out. The total Hamiltonian is then expanded in such a way that it appears in a form that is directly comparable with the usual form of the crystal field Hamiltonian. Antisymmetrized wave functions for the 3 electrons of the system, which are products of atom and molecule functions, are used to calculate the matrix elements of the expanded Hamiltonian. The removal of degeneracy of the 2p state, is compared to that obtained from crystal field theory, and in this way the relationships

are brought out between these matrix elements and the ones of ordinary crystal field theory. The expansion of the interaction Hamiltonian is crucial to our approach. It results in producing the two-particle terms of the interaction Hamiltonian as products of ~~one~~-particle Hamiltonians. Hence the matrix elements are functions of one-electron integrals only. The effect of the Pauli exclusion principle appears, therefore, in relatively simple form. The particular method of expansion of the interaction Hamiltonian used also eliminates the necessity of evaluating 3-center integrals. This feature may make it feasible to obtain numerical results relatively simply. A descriptive designation of our method could be EH-SA-MO (Expanded Hamiltonian Separated Atom Molecular Orbital) Theory.

Expressions showing the explicit dependence of the energy levels of the system on overlap are given and compared with conventional expressions obtained by crystal field theory methods. In our treatment a new complication appears: The matrix obtained from the expanded Hamiltonian and the product wave functions is not always hermitian<sup>16</sup>. This type of difficulty has been observed by Moffitt<sup>13</sup> in a problem related to ours. The hermiticity can be restored by modifying the matrix elements in a standard way.

## CHAPTER II

## THE INTERACTION HAMILTONIAN

1. The Physical Approximations of the Present Theory. The physical system under investigation consists of a hydrogen atom (with nucleus A) in a 2p electronic state, and a hydrogen molecule (with nuclei B and C) in the ground state. The interactions of these two species will be studied. We assume all nuclear positions to be fixed, thus ignoring the important effects of vibrations and rotations on certain aspects of the problem, such as transition probabilities.

A special problem is presented by the overlap of the electron clouds. In problems where it is appropriate to treat the interactions of two species as the interactions of two non-overlapping charge distributions, a straight forward and simple procedure exists. If the charge distributions do overlap, then the calculations are usually separated into several parts which correspond to different regions of convergence. This approach is discussed exhaustively by Hirschfelder, Curtiss and Byrd<sup>17</sup>. In the present treatment we wish to make a compromise, for the sake of simplicity. On the one hand we use quantum mechanical wave functions for the atom and the molecule, and these wave functions certainly overlap. In fact some of the basic results obtained depend on this overlap. On the other hand, we wish to expand the Hamiltonian expressing the interaction between the atom and molecule in a way which exhibits its similarity with the crystal field Hamiltonian. We, therefore, limit

ourselves in the expansion to a region which is equivalent to the zero-overlap region, as discussed by Hirschfelder, et. al. In this way we obtain a manageable result, at the cost of some consistency. It should be pointed out that this same inconsistency pervades the whole of conventional crystal field theory.

When we carry out the expansion of the Hamiltonian in Section II.4, we make the following assumptions: (See Figure 1 for definition of the variables.)

For all expansions we assume that  $r_{AB}$  and  $r_{AC}$  are each larger than  $r_{BC}$ , i.e. that the atom is well separated from the molecule.

In the expansions of the electron coordinates we assume:

$$\text{For } r_{1A}: r_{1A} < r_{AB} \text{ or } r_{AC}$$

II.1

$$\begin{aligned} \text{For } r_{12}: r_{1A} + r_{2B} &< r_{AB} \\ r_{1A} + r_{3C} &< r_{AC} \end{aligned}$$

The assumptions for  $r_{12}$  are the usual ones made in considering Van der Waals interactions of non-overlapping charge distributions<sup>17</sup>. The assumptions for  $r_{1A}$  are somewhat weaker than the former. The consequences of these assumptions are worked out in Section 4, and analyzed briefly in Section 5.

2. The Hamiltonian for the System H - H<sub>2</sub>. We write the Hamiltonian in the following convenient way:

$H_H$  = The Hamiltonian of the free atom

$H_M$  = The Hamiltonian of the free molecule

$H_{INT}$  = The interaction Hamiltonian between the atom and the molecule

$$H_H = -\hbar^2/2m \nabla_1^2 - e^2/r_{1A}$$

$$H_M = -\hbar^2/2m \nabla_2^2 - \hbar^2/2m \nabla_3^2 - e^2/r_{2B} - e^2/r_{2C} \\ - e^2/r_{3B} - e^2/r_{3C} + e^2/r_{BC} + e^2/r_{23}$$

II.2

$$H_{INT} = -e^2/r_{2A} - e^2/r_{3A} - e^2/r_{1B} - e^2/r_{1C} \\ + e^2/r_{12} + e^2/r_{13} + e^2/r_{AB} + e^2/r_{AC} .$$

An interchange of any 2 electrons does not leave  $H_{INT}$  invariant. But in the calculation of matrix elements we only use the total Hamiltonian and this is properly invariant under interchange of any 2 electrons. Let us write the Hamiltonian in a slightly different way where the dependence of the parts on the electron label has been emphasized:

$$H_{TOTAL} = H_H(1) + H_M(2,3) + H_{INT}(1;2,3) . \quad \text{II.3}$$

We expand the interaction Hamiltonian in a certain way which is described in Section II.4, making use of the inequalities of equation (I.1). Then we group together the expansions of different order in the coordinates of the electron of the H atom. The matrix obtained from this expansion shows directly the relationship between crystal field theory and molecular orbital theory.

The solution to Schroedinger's equation without the interaction term is, by definition, denoted as the zeroth order eigenfunction. If we eliminate  $H_{INT}(1;2,3)$  from  $H_{TOTAL}$  then the solution to this

zeroth order Schroedinger equation would be  $\Psi_H(1) \Psi_M(2,3)$ , where  $\Psi_H(1)$  and  $\Psi_M(2,3)$  are eigenfunctions of  $H_H(1)$ , and  $H_M(2,3)$  respectively. ( $\Psi_H$  can take on the specific forms  $2p_x$ ,  $2p_y$  and  $2p_z$ , i.e.  $n = 2$ ,  $l = 1$ , with three components.) This is not an acceptable solution, since it is not antisymmetric on interchange of electrons 1 and 2, for instance. We can, of course, construct a wave function antisymmetric in the three electrons:

$$\Psi_x = N_x 3^{-\frac{1}{2}} [2p_x(1)\Psi_M(2,3) + 2p_x(2)\Psi_M(3,1) + 2p_x(3)\Psi_M(1,2)] \quad \text{II.4}$$

where  $\Psi_M$  is the molecular zero-order eigenfunction, which is assumed antisymmetric in its two electrons and  $N_x$  is a normalization factor. Two other functions,  $\Psi_y$  and  $\Psi_z$ , formed with  $2p_y$  and  $2p_z$  respectively, also occur. We note that  $\Psi$  cannot strictly be a zeroth order eigenfunction since  $\Psi_H$  and  $\Psi_M$  are not orthogonal. We are not really applying perturbation theory; instead we ask: Given  $\Psi_H$  and  $\Psi_M$  as correct eigenfunctions of the Hamiltonian of the atom and the molecule when they are far apart, how are the states changed when one brings the particles together? How do the energies of atomic states change as a function of distance and orientation? We do not investigate in this work how the molecular states are affected, but reserve this for later work. Margenau has investigated<sup>18</sup> the  $H_2 - H$  problem, using a zeroth order eigenfunction completely different from ours, namely functions of spin bond type, constructed of  $1s$  orbitals. In this treatment the H atom is in the ground state, and no comparison with crystal field theory is possible.

3. Notation. In this section, we introduce special notations to facilitate the discussion.  $x_{iM}$  is the x coordinate of the ith electron with respect to nucleus M. Similarly the coordinate  $x_{MN}$  represents the x coordinate of nucleus M with respect to nucleus N.  $x_{BC}(=r_{BC}), x_{AC}, y_{AC}, y_{AB}, r_{AB}, r_{AC}$  are constants. The sign conventions for the vectors  $\vec{r}_{1A}, \vec{r}_{2B}, \vec{r}_{3C}$ , etc. are indicated in Figure 1.

---

The three atoms are assumed to lie in the xy plane. The following relations are typical:

---

$$r_{AB} = \left\{ (x_A - x_B), (y_A - y_B), (z_A - z_B) \right\}$$

$$x_{1B} = x_{AB} + x_{1A}$$

$$x_{1C} = x_{AC} + x_{1A}$$

$$y_{1B} = y_{AB} + y_{1A}$$

$$y_{1C} = y_{AC} + y_{1A}$$

II.5

$$z_{1B} = z_{1A}$$

$$z_{1C} = z_{1A}$$

$$x_{2A} = -x_{AC} + x_{2C}$$

$$y_{2A} = -y_{AB} + y_{2B}$$

$$x_{2A} = -x_{AB} + x_{2B}$$

$$y_{3A} = -y_{AC} + y_{3C}$$

$$z_{2A} = z_{2B}$$

$$z_{3A} = z_{3C}$$

$$x_{12} = x_{1A} + x_{AB} - x_{2B}$$

$$x_{13} = x_{1A} + x_{AC} - x_{3C}$$

II.6

$$y_{12} = y_{1A} + y_{AB} - y_{2B}$$

$$y_{13} = y_{1A} + y_{AC} - y_{3C}$$

$$z_{12} = z_{1A} - z_{2B}$$

$$z_{13} = z_{1A} - z_{3C}$$

$$r_{1B}^2 = r_{1A}^2 + r_{AB}^2 + 2\vec{r}_{1A} \cdot \vec{r}_{AB}$$

II.6

$$r_{1C}^2 = r_{1A}^2 + r_{AC}^2 + 2\vec{r}_{1A} \cdot \vec{r}_{AC}$$

$$r_{12}^2 = (x_{1A} - x_{2B} + x_{AB})^2 + (y_{1A} - y_{2B} + y_{AB})^2 + (z_{1A} - z_{2B})^2$$

$$r_{2A}^2 = r_{2B}^2 + r_{AB}^2 - 2\vec{r}_{2B} \cdot \vec{r}_{AB}$$

$$r_{3A}^2 = r_{3C}^2 + r_{AC}^2 - 2\vec{r}_{3C} \cdot \vec{r}_{AC}$$

We also denote by special symbols important functions of the coordinates:

$$\alpha = x_{AB}r_{AB}^{-2}$$

$$\beta = y_{AB}r_{AB}^{-2}$$

II.7

$$\gamma = x_{AC}r_{AC}^{-2}$$

$$\delta = y_{AC}r_{AC}^{-2}$$

$$u = x_{1A}r_{1A}^{-2}$$

II.8

$$v = y_{1A}r_{1A}^{-2}$$

$$V_{1A} = \alpha x_{1A} + \beta y_{1A}$$

$$V_{2B} = \alpha x_{2B} + \beta y_{2B}$$

$$U_{3C} = \gamma x_{3C} + \delta y_{3C}$$

II.9

$$U_{1A} = \gamma x_{1A} + \delta y_{1A}$$

$$W_{AB} = x_{AB}^u + y_{AC}^v$$

$$W_{AC} = x_{AC}^u + y_{AC}^v$$

II.10

$$W_{2B} = x_{2B}^u + y_{2B}^v$$

$$W_{3C} = x_{3C}^u + y_{3C}^v$$

4. The Expansion. We give here <sup>the</sup> expansion of  $H_{INT}$  for the conditions of equation II.1. We recall from sections II.2, and II.3 the notation and relationships given there, and the expression for  $H_{INT}$ , and proceed to expand  $H_{INT}$  in the following way. We first rewrite some of the expressions of section II.3 (cf. Eq. II.6):

$$r_{1B}^{-1} = [r_{1A}^2 + r_{AB}^2 + 2\vec{r}_{1A} \cdot \vec{r}_{AB}]^{-\frac{1}{2}} = r_{AB}^{-1} [1 + r_{1A}^2 r_{AB}^{-2} + 2\vec{r}_{1A} \cdot \vec{r}_{AB} r_{AB}^{-2}]^{-\frac{1}{2}}$$

$$r_{1C}^{-1} = [r_{1A}^2 + r_{AC}^2 + 2\vec{r}_{1A} \cdot \vec{r}_{AC}]^{-\frac{1}{2}} = r_{AC}^{-1} [1 + r_{1A}^2 r_{AC}^{-2} + 2\vec{r}_{1A} \cdot \vec{r}_{AC} r_{AC}^{-2}]^{-\frac{1}{2}} \quad \text{II.11}$$

$$r_{2A}^{-1} = [r_{2B}^2 + r_{AB}^2 - 2\vec{r}_{2B} \cdot \vec{r}_{AB}]^{-\frac{1}{2}} = r_{AB}^{-1} [1 + r_{2B}^2 r_{AB}^{-2} - 2\vec{r}_{2B} \cdot \vec{r}_{AB} r_{AB}^{-2}]^{-\frac{1}{2}}$$

$$\begin{aligned}
r_{3A}^{-1} &= [r_{3C}^2 + r_{AC}^2 - 2\vec{r}_{3C} \cdot \vec{r}_{AC}]^{-\frac{1}{2}} = r_{AC}^{-1} [1 + r_{3C}^2 r_{AC}^{-2} - 2\vec{r}_{3C} \cdot \vec{r}_{AC} r_{AC}^{-2}]^{-\frac{1}{2}} \\
r_{12}^{-1} &= r_{AB}^{-1} [1 + (\vec{r}_{1A} - \vec{r}_{2B}) \cdot (\vec{r}_{1A} - \vec{r}_{2B}) r_{AB}^{-2} + 2(\vec{r}_{1A} - \vec{r}_{2B}) \cdot \vec{r}_{AB} r_{AB}^{-2}]^{-\frac{1}{2}} \quad \text{II.11} \\
r_{13}^{-1} &= r_{AC}^{-1} [1 + (\vec{r}_{1A} - \vec{r}_{3C}) \cdot (\vec{r}_{1A} - \vec{r}_{3C}) r_{AC}^{-2} + 2(\vec{r}_{1A} - \vec{r}_{3C}) \cdot \vec{r}_{AC} r_{AC}^{-2}]^{-\frac{1}{2}}.
\end{aligned}$$

To make clearer the nature of the expansion for the first 4 expressions, we write out  $r_{1B}^{-1}$  in full detail. Thus,

$$r_{1B}^{-1} = r_{AB}^{-1} [1 + (x_{1A}^2 + y_{1A}^2 + z_{1A}^2) r_{AB}^{-2} + 2(x_{1A}x_{AB} + y_{1A}y_{AB}) r_{AB}^{-2}]^{-\frac{1}{2}}.$$

We now assume  $r_{1A} < r_{AB}$  (cf. Eq. II.1); hence,  $r_{1A}^2 r_{AB}^{-2}$  is a second order quantity in  $r_{1A}/r_{AB}$ . Let us write  $r_{1B}^{-1} = r^{-1} [1 + y^2 + x]^{-\frac{1}{2}}$ , where  $y^2 = r_{1A}^2 r_{AB}^{-2}$  and  $x = (x_{1A}x_{AB} + y_{1A}y_{AB}) r_{AB}^{-2}$ . We expand  $[1 + y^2 + x]^{-\frac{1}{2}}$  in a power series of  $(y^2 + x)$ , and we group the terms according to their order of magnitude. Although  $y^2$  and  $x$  represent quantities of different orders of magnitude,  $y^2 + x < 1$  assures the convergence of the Taylor Series expansion of  $(1 + y^2 + x)^{-\frac{1}{2}}$  in powers of  $y^2 + x$ . The general result is given in Appendix A. In the expression for  $r_{12}$ , we regard  $(\vec{r}_{1A} - \vec{r}_{2B}) \cdot (\vec{r}_{1A} - \vec{r}_{2B}) r_{AB}^{-2}$  as a second order quantity in  $|\vec{r}_{1A} - \vec{r}_{2B}| r_{AB}^{-1}$ , and  $(x_{1A} - x_{2B}) x_{AB} r_{AB}^{-2} + r_{AB}^{-2} (y_{1A} - y_{2B}) y_{AB}$  as a first order quantity in  $|\vec{r}_{1A} - \vec{r}_{2B}| r_{AB}^{-1}$  (cf. Eq. II.1). The result of the expansion is given below, where we have grouped together terms of the same order of magnitude.

To simplify the discussion we adopt the following convention: We group terms in the expansion of  $H_{INT}$  by their order in the expansion, and then collect the terms of a given degree in the electron coordinates measured from the atom. We shall use order and degree only in the sense just given. The zeroth order term:

$$e^2 [-r_{AB}^{-1} - r_{AC}^{-1} - r_{AB}^{-1} - r_{AC}^{-1} + 2r_{AB}^{-1} + 2r_{AC}^{-1}] = 0 .$$

The first order term:

$$e^2 [\vec{r}_{1A} \cdot \vec{r}_{AB} r_{AB}^{-3} + \vec{r}_{1A} \cdot \vec{r}_{AC} r_{AC}^{-3} - \vec{r}_{2B} \cdot \vec{r}_{AB} r_{AB}^{-3} - \vec{r}_{3C} \cdot \vec{r}_{AC} r_{AC}^{-3} - (\vec{r}_{1A} - \vec{r}_{2B}) \cdot \vec{r}_{AB} r_{AB}^{-3} - (\vec{r}_{1A} - \vec{r}_{3C}) \cdot \vec{r}_{AC} r_{AC}^{-3}] = 0 .$$

We have shown explicitly the grouping of terms for the zeroth and 1st order of the expansion. The physical significance of their vanishing means that up to, but not including, second order terms, the hydrogen atoms appear to the hydrogen molecule and vice-versa as uncharged objects without dipole moment. We must go to second order terms to find any interaction at all. The various orders of the expansions are presented in vector notation in Table II.1. The detailed cartesian form of these expansions which show the resemblance of our treatment to the expansions of crystal field theory is shown in Appendix B. It is striking that the 2nd order terms of the expansion contain only linear terms in  $x_{1A}$ . In conventional crystal field theory they would contribute only through configuration interaction. To find terms

TABLE II.1

Expansion of  $H_{INT}(1,2,3)$ 

Second Order Terms:

$$(\vec{r}_{1A} \cdot \vec{r}_{2B})r_{AB}^{-3} + (\vec{r}_{1A} \cdot \vec{r}_{3C})r_{AC}^{-3} - 3V_{1A}V_{2B}r_{AB}^{-1} - 3U_{1A}U_{3C}r_{AC}^{-1}.$$

Third Order Terms:

$$\frac{3}{2} \left\{ \begin{aligned} & r_{AB}^{-3} [V_{1A}r_{2B}^2 - V_{2B}r_{1A}^2 - 2(V_{1A} - V_{2B})\vec{r}_{1A} \cdot \vec{r}_{2B}] \\ & + r_{AC}^{-3} [U_{1A}r_{3C}^2 - U_{3C}r_{1A}^2 - 2(U_{1A} - U_{3C})\vec{r}_{1A} \cdot \vec{r}_{3C}] \end{aligned} \right\}$$

$$+15/2 [r_{AB}^{-1}V_{1A}V_{2B}(V_{1A} - V_{2B}) + r_{AC}^{-1}U_{1A}U_{3C}(U_{1A} - U_{3C})].$$

Fourth Order Terms:

$$-3/4 \left\{ \begin{aligned} & r_{AB}^{-5} [2\vec{r}_{1A} \cdot \vec{r}_{2B}(r_{1A}^2 + r_{2B}^2 - \vec{r}_{1A} \cdot \vec{r}_{2B}) - r_{1A}^2 r_{2B}^2] \\ & r_{AC}^{-5} [2\vec{r}_{1A} \cdot \vec{r}_{3C}(r_{1A}^2 + r_{3C}^2 - \vec{r}_{1A} \cdot \vec{r}_{3C}) - r_{1A}^2 r_{3C}^2] \end{aligned} \right\}$$

$$+15/4 \left\{ \begin{aligned} & r_{AB}^{-3} [2\vec{r}_{1A} \cdot \vec{r}_{2B}(V_{1A} - V_{2B})^2 + r_{1A}^2 V_{2B}(2V_{1A} - V_{2B}) + r_{2B}^2 V_{1A}(2V_{2B} - V_{1A})] \\ & + r_{AC}^{-3} [2\vec{r}_{1A} \cdot \vec{r}_{3C}(U_{1A} - U_{3C})^2 + r_{1A}^2 U_{3C}(2U_{1A} - U_{3C}) + r_{3C}^2 U_{1A}(2U_{3C} - U_{1A})] \end{aligned} \right\}$$

$$-35/4 \left\{ \begin{aligned} & r_{AB}^{-1}V_{1A}V_{2B}(2V_{1A}^2 - 3V_{1A}V_{2B} + 2V_{2B}^2) \\ & + r_{AC}^{-1}U_{1A}U_{3C}(2U_{1A}^2 - 3U_{1A}U_{3C} + 2U_{3C}^2) \end{aligned} \right\}.$$

quadratic in  $x_{Ai}$  one must go to third order terms. Then we find that in the latter only linear functions of the molecular electrons coordinates  $x_{Bi}$ , and  $x_{Ci}$  arise. Hence, averages of these over unperturbed molecular functions will vanish. Thus, we must go to the fourth order expansion to find large effects on the atomic levels.

5. Critique of the Expansion of Section II.4. In expanding  $H_{INT}(1;2,3)$  one must sum the following terms:  $e^2 [\sum_{i,M} -r_{iM}^{-1} + \sum_{i>j} r_{ij}^{-1}]$ . It is clear that the first sum has different converging properties than the second. For instance, the expansion for  $r_{2A}^{-1}$  given in the last section converges for  $0 < r_{1A} < r_{AB}$ , while that for  $r_{12}^{-1}$  converges in the region  $0 < r_{1A} < r_{AB} - r_{2B}$ . Thus, the expansion of  $H_{INT}(1;2,3)$  given in Section II.4 is strictly correct only in the region of  $0 < r_{1A} < r_{AB} - r_{2B}$ .

We summarize now the converging expansions of attraction and repulsion terms appearing in  $H_{INT}(1;2,3)$ . We consider the typical sum  $-r_{2A}^{-1} - r_{1B}^{-1} + r_{12}^{-1}$  ( $r_{2B}$  again is understood always to be less than  $r_{AB}$ ) and define the regions of converging expansions:

a)  $r_{2A}^{-1}$  and  $r_{1B}^{-1}$

Expansion A converges provided  $r_{1A} < r_{AB}$

Expansion B converges provided  $r_{1A} > r_{AB}$

b)  $r_{12}^{-1}$

Expansion A' converges provided  $0 < r_{1A} < r_{AB} - r_{2B}$

Expansion B' converges provided  $0 < r_{AB} - r_{2B} < r_{1A} < r_{AB}$

Expansion C' converges provided  $r_{AB} < r_{1A} < r_{AB} + r_{2B}$

Expansion D' converges provided  $r_{AB} + r_{2B} < r_{1A} < \infty$

We now describe the 4 regions and indicate how the different sums should be added.

| Region     | Condition                           | Expansion |
|------------|-------------------------------------|-----------|
| Region I   | $0 < r_{1A} < r_{AB} - r_{2B}$      | A + A'    |
| Region II  | $r_{AB} - r_{2B} < r_{1A} < r_{AB}$ | A + B'    |
| Region III | $r_{AB} < r_{1A} < r_{AB} + r_{2B}$ | B + C'    |
| Region IV  | $r_{AB} + r_{2B} < r_{1A} < \infty$ | B + D' .  |

In the detailed calculations of the interactions of the H atom and H<sub>2</sub> molecule, we confine ourselves to the "easy" region I of the expansion. The results for the region I can be related in detail to ordinary crystal field theory. For the sake of illustrating the complexities which arise in the expansions for the other regions, we present in the next few pages details for the expansions B and B'. The attraction and repulsion terms are rewritten so that the expansion is readily made in the region of interest here. The factor e<sup>2</sup> has been omitted for simplicity. Then, H<sub>INT</sub>(1;2,3) contains the terms:

$$-r_{1B}^{-1} = -r_{1A}^{-1} \left[ 1 + r_{AB}^2 r_{1A}^{-2} + \frac{1}{2r_{1A}} \cdot \frac{1}{r_{AB} r_{1A}} r_{AB}^{-2} \right]^{-\frac{1}{2}}$$

$$-r_{1C}^{-1} = -r_{1A}^{-1} \left[ 1 + r_{AC}^2 r_{1A}^{-2} + \frac{1}{2r_{1A}} \cdot \frac{1}{r_{AC} r_{1A}} r_{AC}^{-2} \right]^{-\frac{1}{2}}$$

$$-r_{2A}^{-1} = -r_{AB}^{-1} \left[ 1 + r_{2B}^2 r_{AB}^{-2} - \frac{1}{2r_{2B}} \cdot \frac{1}{r_{AB} r_{AB}} r_{AB}^{-2} \right]^{-\frac{1}{2}}$$

$$\begin{aligned}
- r_{3A}^{-1} &= -r_{AC}^{-1} [1 + r_{3C}^2 r_{AC}^{-2} - 2\vec{r}_{3C} \cdot \vec{r}_{AC} r_{AC}^{-2}]^{-\frac{1}{2}} \\
+ r_{12}^{-1} &= r_{1A}^{-1} [1 + 2(\vec{r}_{AB} - \vec{r}_{2B}) \cdot \vec{r}_{1A} r_{1A}^{-2} + (\vec{r}_{AB} - \vec{r}_{2B}) \cdot (\vec{r}_{AB} - \vec{r}_{2B}) r_{1A}^{-2}]^{-\frac{1}{2}} \\
+ r_{13}^{-1} &= r_{1A}^{-1} [1 + 2(\vec{r}_{AC} - \vec{r}_{3C}) \cdot \vec{r}_{1A} r_{1A}^{-2} + (\vec{r}_{AC} - \vec{r}_{3C}) \cdot (\vec{r}_{AC} - \vec{r}_{3C}) r_{1A}^{-2}]^{-\frac{1}{2}} \\
+ r_{AB}^{-1} &+ r_{AC}^{-1} .
\end{aligned}$$

The last 2 terms represent the nuclear repulsion between the atom and the molecule and are constants in the problem. The zeroth order terms are:

$$- r_{1A}^{-1} - r_{1A}^{-1} - r_{AB}^{-1} - r_{AC}^{-1} + r_{1A}^{-1} + r_{1A}^{-1} + r_{AB}^{-1} + r_{AC}^{-1} = 0 .$$

The first order terms:

$$r_{1A}^{-3} \vec{r}_{1A} \cdot [\vec{r}_{2B} + \vec{r}_{3C}] - r_{AB}^{-3} \vec{r}_{2B} \cdot \vec{r}_{AB} - r_{AC}^{-3} \vec{r}_{3C} \cdot \vec{r}_{AC} \neq 0 .$$

Second order terms: In order to perform the expansion more easily, we use the notation of section II.3. The expression for  $H_{INT}$  thus becomes:

$$\begin{aligned}
- r_{1B}^{-1} &= -r_{1A}^{-1} [1 + r_{AB}^2 r_{1A}^{-2} + 2W_{AB}]^{-\frac{1}{2}} \\
- r_{1C}^{-1} &= -r_{1A}^{-1} [1 + r_{AC}^2 r_{1A}^{-2} + 2W_{AC}]^{-\frac{1}{2}} \\
- r_{2A}^{-1} &= -r_{AB}^{-1} [1 + r_{2B}^2 r_{AB}^{-2} - 2V_{2B}]^{-\frac{1}{2}} \\
- r_{3A}^{-1} &= -r_{AC}^{-1} [1 + r_{3C}^2 r_{AC}^{-2} - 2U_{3C}]^{-\frac{1}{2}}
\end{aligned}$$

$$+ r_{12}^{-1} = r_{1A}^{-1} [1 + (\vec{r}_{AB} - \vec{r}_{2B}) \cdot (\vec{r}_{AB} - \vec{r}_{2B}) r_{1A}^{-2} + 2(W_{AB} - W_{2B})]^{-\frac{1}{2}}$$

$$+ r_{13}^{-1} = r_{1A}^{-1} [1 + (\vec{r}_{AC} - \vec{r}_{3C}) \cdot (\vec{r}_{AC} - \vec{r}_{3C}) r_{1A}^{-2} + 2(W_{AC} - W_{3C})]^{-\frac{1}{2}}$$

Using the Taylor series, Appendix A, we find the 2nd order expansion to be of the form  $-\frac{1}{2} y^2 + 3/8 x^2$ . We collect the various terms, and simplify to obtain:

$$-\frac{1}{2} y^2 = \frac{1}{2} r_{1A}^{-3} [r_{2B}^2 + r_{3C}^2 - 2\vec{r}_{AB} \cdot \vec{r}_{2B} - 2\vec{r}_{AC} \cdot \vec{r}_{3C}] + \frac{1}{2} r_{AB}^{-3} r_{2B}^2 + \frac{1}{2} r_{AC}^{-3} r_{3C}^2$$

$$3/8 x^2 = 3/2 r_{1A}^{-1} [(W_{2B})^2 + (W_{3C})^2 - 2W_{AB}W_{2B} - 2W_{AC}W_{3C}] - 3/2 r_{AB}^{-1} V_{2B}^2 - 3/2 r_{AC}^{-1} U_{3C}^2$$

The third and fourth order expansions will be found in Appendix C. Some conclusions can now be reached. We see here that the first order terms no longer vanish. If we look at the members we find that  $r_{1A}$  appears in the denominator. Thus, as we integrate from  $(r_{AB} \pm r_{2B})$  to  $\infty$  the integral is damped quite considerably beyond  $r_{AB}$  (average of the 2 lower limits of integration). The fact that  $r_{1A}$  occurs in the denominator, makes the overlap integrals between the  $2p_A$  and  $1s_B$  function (out of which  $\psi_M$  is constructed) behave beyond the region  $r_{1A} = r_{AB}$  as if the  $2p$  electron is in a  $1s$  state. In such a case, the overlap integral from  $r_{AB}$  to  $\infty$

in the  $r$ -integration does not contribute very much. This argument applies even more strongly to the higher order terms in the expansion. We therefore conclude that reasonable accuracy could be obtained if we cut off the  $r$ -integration at a distance where the overlap is not appreciable between  $1s$  electrons belonging to the different systems. This is discussed in Reference 16.

As was pointed out above, in our detailed considerations throughout the paper we ignore the difficulties just discussed, by limiting ourselves to the "easy" region of the expansion. It is useful to point out that similar problems of convergence are ignored in ordinary crystal field theory. There the considerations are also limited to the "easy" region. Such a procedure lacks, of course, any real mathematical rigor. The aim of this paper is to shed light on the nature of the crystal field approximation. We feel, therefore, justified not to reformulate the expansions used in the theory with greater rigor, but to carry out our discussion on the level of rigor customary in the field.

## CHAPTER III

## THE MATRIX ELEMENTS

1. The General Result. We wish to know how the  $H_2$  molecule removes the orbital degeneracy of the  $2p$  state of the hydrogen atom. We have to investigate a  $3 \times 3$  matrix, if we ignore the spins of the atom for the moment. Before we obtain the matrix elements for this problem, we define a set of 3 orthonormal functions for the system:  $2p_x$ ,  $2p_y$ , and  $2p_z$  are normalized hydrogen atomic orbitals. They are centered about nucleus A.

$\alpha(i)$  = spin eigenfunction for  $i$ th electron with  $m_s = +\frac{1}{2}$

$\beta(i)$  = spin eigenfunction for  $i$ th electron with  $m_s = -\frac{1}{2}$

$1s_B(i)$  = ground state hydrogen atom function for  $i$ th electron about nucleus B

$1s_C(i)$  = ground state hydrogen atom function for  $i$ th electron about nucleus C.

The choice of molecular functions poses a certain problem. It is clear that one could take here the point of view that any molecular function can be used which gives good numerical results, for example an elaborate self-consistent field function. We wish, however, to get a simple result whose significance can be understood readily, and we are not primarily interested in numerical accuracy, at least at present.

Therefore, we have limited ourselves to a molecular function which is built up from a product of one-electron functions. This would be achieved either by a valence-bond or a molecular orbital function.

The valence-bond function is simpler, and would give better results at long separations of the nuclei of the molecule. But the molecular orbital function gives slightly better results for the actual molecule. An additional reason is the following: The MO type function may give rise to terms in the final result which are of interest (i.e. those arising from the ionic structures for the molecule), even though these terms are not given the proper weight in the result. A valence bond function would omit such terms altogether. In the derivations given below the molecular wave function is kept general as long as possible. We use

$$\Psi_M(2,3) = N_M [1s_B(2) + 1s_C(2)][1s_B(3) + 1s_C(3)] 2^{-\frac{1}{2}} [\alpha(2)\beta(3) - \alpha(3)\beta(2)]$$

III.

$$\Psi_x(1,2,3) = 3^{-\frac{1}{2}} N_x [2p_x(1)\alpha(1)\Psi_M(2,3) + 2p_x(2)\alpha(2)\Psi_M(3,1) + 2p_x(3)\alpha(3)\Psi_M(1,2)]$$

$N_M$ ,  $N_x$ , etc., are normalizing constants. See Appendix D.

$\Psi_y$  and  $\Psi_z$  are obtained by replacing x by y, and z, respectively.

$\Psi_i$  stands for  $\Psi_x$ ,  $\Psi_y$ , and  $\Psi_z$ , as  $i = 1, 2$ , and  $3$  respectively.

$\Phi_I$ ,  $\Phi_{II}$ , and  $\Phi_{III}$  are an orthonormalized set of functions constructed

out of the 3 independent functions  $\Psi_x$ ,  $\Psi_y$ , and  $\Psi_z$ . Details are

found in Appendix E. To avoid confusion:  $(\Psi_{A,i} | \Psi_{A,i})$  refers to

integration over one electron orbital only,  $\Psi_{A,i}$  refers to

the  $i$ th atomic orbital about nucleus A.  $\Psi_{BC}$  is defined as the

function  $(1s_B + 1s_C) N_M^{-\frac{1}{2}}$ , which has the normalizing factor  $N_M^{-\frac{1}{2}}$ .

The following is an important product of overlap integrals:

$a_{ij} = (2p_{A,i} | \psi_{BC}) (\psi_{BC} | 2p_{A,j})$ . As the index  $i$  runs from one to three,  $2p_{A,i}$  refers to the  $2p_x$ ,  $2p_y$ , and  $2p_z$  atomic orbitals respectively.

Throughout the present calculation we shall take the spin of the H atom to be  $+\frac{1}{2}$ . The doublet spin degeneracy is, of course, not lifted in this problem. The set of orthonormalized functions is chosen as follows:

$$\Phi_I = \psi_x$$

$$\Phi_{II} = (a_{12} \Phi_I + \psi_y) (1 - a_{12}^2)^{-\frac{1}{2}} \quad \text{III.2}$$

$$\Phi_{III} = \psi_z$$

The general result of the calculation of the matrix elements of the total Hamiltonian, using the expansion of Section II.4 (Region I), and the functions of equation III.1 is this:

$$(\psi_i | H_T | \psi_j) =$$

$$= N_i N_j \left[ \begin{aligned} & (E_H + E_M) (\delta_{ij} - a_{ij}) \\ & + \sum_{k,l,m} (2p_{A,i} | H_A^{kl} | 2p_{A,j}) (\psi_{BC} | H_B^{ml} + H_C^{ml} | \psi_{BC}) \\ & - \frac{1}{2} (2p_{A,i} | H_B^{ml} + H_C^{ml} | \psi_{BC}) (\psi_{BC} | H_A^{kl} | 2p_{A,j}) \\ & - \frac{1}{2} (2p_{A,i} | \psi_{BC}) (\psi_{BC} | H_B^{ml} + H_C^{ml} | \psi_{BC}) (\psi_{BC} | H_A^{kl} | 2p_{A,j}) \end{aligned} \right] \quad \text{III.3}$$

Here:  $H_A^{kl}$  is the  $l$ -th term of a homogeneous polynomial of  $k$ -th degree in coordinates centered on A;

$H_B^{ml}$  is the  $l$ -th term of a homogeneous polynomial of  $m$ -th degree in coordinates centered on B, and multiplies the  $l$ -th term  $H_A^{kl}$ ;

$H_C^{ml}$  is the  $l$ -th term of a homogeneous polynomial of the  $m$ -th degree in the coordinates centered on C, multiplying the  $l$ -th term  $H_A^{kl}$ .

Each of the polynomials contains constant coefficients involving powers of internuclear distance in such a way that the total product has the correct dimension of energy. The details of this are developed below. The proof for this result up to and including fourth order terms of  $H_{INT}$  will be found below, and in Appendix F. The simple result of equation III.3 depends strongly on the following argument. Examination of the result of the expansion of  $H_{INT}$  (Section II.4 and Appendix B) shows that the result of the expansion may be summarized as follows:

$$H_{INT} = \sum_{k,l,m} H_A^{kl} (H_B^{ml} + H_C^{ml}) . \quad \text{III.4}$$

The nature of the terms  $H_A^{kl}$ , etc., is explained above. The details of their structure can be seen in Appendix B. No electron labels appear in this expression for the interaction Hamiltonian, because all interaction terms are expanded into one-electron Hamiltonians. Furthermore, these one-electron terms are transformed in such a way (by means of expressions of type II.5 and II.6) that the coordinates of electron 1 always refer to the origin at A, those of electron 2 to the origin at B,

and those of electron 3 to the origin at C. The wave functions are products of one-electron wave functions. Therefore all integrals can be transformed into one-electron integrals, and these are, of course, independent of electron labels. It should be noted that this great simplification arises from the method of expansion used here. The Pauli principle is still taken into account, however, since the total Hamiltonian is a symmetric function of the electron labels, and the wave functions are antisymmetric functions of the electron labels. The general significance of this very interesting simplification is not fully worked out at present.

We can give the matrix elements  $(\Phi_i | H_T | \Phi_j)$  in terms of the  $(\psi_i | H_T | \psi_j)$  described above.

$$(\Phi_I | H_T | \Phi_I) = (\psi_1 | H_T | \psi_1)$$

$$(\Phi_{II} | H_T | \Phi_{II}) = (1 - a_{12}^2)^{-1} [a_{12}^2 (\psi_1 | H_T | \psi_1) + 2a_{12} (\psi_1 | H_T | \psi_2) + (\psi_2 | H_T | \psi_2)]$$

$$(\Phi_{III} | H_T | \Phi_{III}) = (\psi_3 | H_T | \psi_3)$$

$$(\Phi_I | H_T | \Phi_{II}) = (1 - a_{12}^2)^{-\frac{1}{2}} [a_{12} (\psi_1 | H_T | \psi_1) + (\psi_1 | H_T | \psi_2)]$$

$$(\Phi_I | H_T | \Phi_{III}) = (\psi_1 | H_T | \psi_3)$$

$$(\Phi_{II} | H_T | \Phi_{III}) = (1 - a_{12}^2)^{-\frac{1}{2}} [a_{12} (\psi_1 | H_T | \psi_3) + (\psi_2 | H_T | \psi_3)] .$$

The influence of overlap in the expressions for the matrix elements should be noted. The overlap between the atomic and molecular functions causes the mixing of the atomic orbitals regardless of the strength or nature of the interaction Hamiltonian.

There are 2 special orientations of the H atom with respect to the molecular axis of symmetry of the  $H_2$  in which  $(\Phi_i | H_T | \Phi_j)$  reduces to  $(\psi_i | H_T | \psi_j)$ . This affords a great simplification in our analysis and therefore they will be discussed next. In one orientation the H atom is situated along the molecular axis of symmetry (linear model). Here, only  $a_{11} \neq 0$  because  $(2p_y | \psi_{BC}) = 0$  and  $(2p_z | \psi_{BC}) = 0$ , from symmetry considerations. We call this model the linear model.

In the other case the H atom is situated on the perpendicular bisectrix of the internuclear axis of the molecule (T model). Here  $H_B^{ml}$  has the same functional dependence on the coordinates centered on B as  $H_C^{ml}$  has on those centered on C. Again, only  $a_{22} \neq 0$  because  $(2p_x | \psi_{BC}) = (2p_z | \psi_{BC}) = 0$  from symmetry considerations. In these 2 cases the matrix elements of  $H_T$  can be written as follows:

$$\begin{aligned}
 (\psi_i | H | \psi_j) &= (E_H + E_M) \delta_{ij} + N_i N_j \sum_{k,m,\ell} (2p_{A,i} | H_A^{k\ell} | 2p_{A,j}) (\psi_{BC} | H_B^{m\ell} + H_C^{m\ell} | \psi_{BC}) \\
 &\quad - \frac{1}{2} (2p_{A,i} | H_B^{m\ell} + H_C^{m\ell} | \psi_{BC}) (\psi_{BC} | H_A^{k\ell} | 2p_{A,j}) \quad \text{III} \\
 &\quad - \frac{1}{2} (2p_{A,i} | \psi_{BC}) (\psi_{BC} | H_B^{m\ell} + H_C^{m\ell} | \psi_{BC}) (\psi_{BC} | H_A^{k\ell} | 2p_{A,j})
 \end{aligned}$$

Let us further write the matrix  $H_{ij}$  as the sum of 3 other matrices to facilitate the discussion.

$$H_{ij} = H_{ij}^{\circ} + N_i N_j H_{ij}^C - \frac{1}{2} N_i N_j H_{ij}^I \quad \text{III}$$

$$\text{where } H_{ij}^{\circ} = (E_H + E_M) \delta_{ij} \quad \text{III}$$

$$H_{ij}^C = \sum_{k,m,\ell} (2p_{A,i} | H_A^{k\ell} | 2p_{A,j}) (\psi_{BC} | H_B^{m\ell} + H_C^{m\ell} | \psi_{BC}) \quad \text{III.8}$$

$$H_{ij}^I = \sum_{k,m,\ell} (2p_{A,i} | H_B^{m\ell} + H_C^{m\ell} | \psi_{BC}) (\psi_{BC} | H_A^{k\ell} | 2p_{A,j}) \\ + (2p_{A,i} | \psi_{BC}) (\psi_{BC} | H_B^{m\ell} + H_C^{m\ell} | \psi_{BC}) (\psi_{BC} | H_A^{k\ell} | 2p_{A,j}) . \quad \text{III.9}$$

$H_{ij}^O$  represents the contribution to the Hamiltonian if the atom and molecule are at an infinite distance from each other.

$H_{ij}^C$  represents terms which we call crystal field type terms: They will be discussed later on in Sections 3a, 3b, and in Chapter IV.

$H_{ij}^I$  represents the effect of the Pauli principle on the 3 interacting electrons, involving products of 2- and 3-center integrals.

The matrix elements, as they appear in Equation III.3 are not always hermitean<sup>16</sup>. This is at first surprising since we are evaluating matrix elements of the hermitean operator  $H_T$ . The difficulty arises because we are satisfying both the Pauli exclusion principle for the electrons and the fact that we assume the chosen molecular wave function to be an eigenfunction of  $H_M$  (cf. II.2). Moffitt<sup>13</sup> encountered the same difficulty in treating a similar problem. But in the special cases we consider, up to and including 4th order terms of the interaction Hamiltonian,  $H_{ij}^I = 0$  for  $i \neq j$ , so that the problem of hermiticity does not arise.

2. More Notation. Certain expressions can be simplified very considerably by adopting additional special notations.

We define, for use with the T model:

$$P_k^\pm = k_B \pm k_C. \quad \text{If } k = x, P_x^+ = x_B + x_C. \quad \text{III.10}$$

$$Q_{kl}^\pm = k_B \hat{\imath}_B \pm k_C \hat{\imath}_C. \quad \text{If } k = y \text{ and } \hat{\imath} = z, \text{ then } Q_{yz}^+ = y_B z_B + y_C z_C. \quad \text{III.11}$$

$$T_{klm}^\pm = k_B \hat{\imath}_B^m \pm k_C \hat{\imath}_C^m. \quad \text{III.12}$$

The symbols  $k, \hat{\imath}$  and  $m$  stand for variables, and can range independently over  $x, y$ , and  $z$ . If the superscript signs are left off, the  $+$  sign will be understood to be present.  $\alpha_k^r, \alpha_{kl}^r, \alpha_k^{rs}, \alpha_{klm}^r, \alpha_{kl}^{rs}$ , and  $\alpha_k^{rst}$  are constant parameters which appear in the interaction Hamiltonian for the T model. These parameters multiply the following terms respectively:  $P_k^r A, Q_{kl}^r A, P_k^r A A, T_{klm}^r A, Q_{kl}^r A A, \text{ and } P_k^r A A A$ . The superscripts for the parameters  $\alpha$  are related to the variables in the factors which the parameters multiply. Thus  $\alpha_k^{12}$  multiplies  $P_k^x y_A$ , and  $\alpha_{122}^3$  multiplies  $T_{xyy}^z A$ . The expression  $\alpha_k^r P_i^\pm$  is an abbreviation for  $\alpha_k^r P_i^+ + \alpha_k^r P_i^-$ , etc.

The interaction Hamiltonian for the T model can then be written in the following special form:

$$\begin{aligned}
 H_{\text{INT}} = & \sum_{k,r} (\alpha_k^r P_k^\pm r_A) + \sum_{k,l,r} (\alpha_{kl}^r Q_{kl}^\pm r_A) \\
 & + \sum_{k,r,s} (\alpha_k^{rs} P_k^\pm r_A s_A) \\
 & + \sum_{k,r,s,t} (\alpha_k^{rst} P_k^\pm r_A s_A t_A) \quad \text{III.13} \\
 & + \sum_{k,l,r,s} (\alpha_{kl}^{rs} Q_{kl}^\pm r_A s_A) \\
 & + \sum_{k,l,m,r} (\alpha_{klm}^r T_{klm}^\pm r_A) + \dots
 \end{aligned}$$

A common factor of  $e^2$  has been omitted in every term.

It can be seen from equation 13 that the interaction Hamiltonian is a sum of terms, in ascending orders of the expansion, and in various degrees in the electron coordinates. In the above expression all electron labels are again superfluous. For the reason see the discussion after equation III.4.

For use with the linear model we introduce the following notation: The constants  $\alpha_{Pk}^r$ ,  $\alpha_{Pkl}^r$ ,  $\alpha_{Pk}^{rs}$ ,  $\alpha_{Pklm}^r$ ,  $\alpha_{Pkl}^{rs}$ ,  $\alpha_{Pk}^{rst}$  multiply certain functions of electron coordinates. The subscript P ranges over the two nuclei B

and C of the molecule. Thus  $\alpha_{Bk}^r$  multiplies  $k_{B^r A}$ , and  $\alpha_{Ck\ell m}^r$  multiplies  $k_C^{\ell m} C_A^r$ . In these expressions  $k, \ell, m, r$  and  $s$  again range over  $x, y$ , and  $z$  as above.

It is then possible to write the interaction Hamiltonian for the linear model in the form:

$$\begin{aligned}
 H_{\text{INT}} = & \sum_{P,k,r} (\alpha_{Pk}^r k_P r_A) + \sum_{P,k,\ell,r} (\alpha_{Pkl}^r k_P \ell_{P^r A}) \\
 & + \sum_{P,k,r,s} (\alpha_{Pk}^{rs} k_P r_A s_A) \\
 & + \sum_{P,k,\ell,m,r} (\alpha_{Pklm}^r k_P \ell_P m_P r_A) \\
 & + \sum_{P,k,\ell,r,s} (\alpha_{Pkl}^{rs} k_P \ell_P r_A s_A) \\
 & + \sum (\alpha_{Pk}^{rst} k_P r_A s_A t_A) + \dots
 \end{aligned}
 \tag{III.14}$$

A common factor of  $e^2$  has been omitted in every term.

3. Analysis of the Matrix Elements. The form of the matrix element (Eq. III.3) together with the expressions for the Hamiltonian (Eq. III.13 and III.14) enable us to make a direct comparison with the matrix elements obtained by crystal field theory methods. As was already explained above (Eq. III.6, 7, 8, 9), we are able to show that the matrix elements consist of 3 distinctive parts. The first part represents the zeroth

order energy when the 2 interacting systems are at infinite distance from each other. The second part contains terms which are analogous to crystal field theory matrix elements, which can be shown to include a dependence on the overlap between the atomic and the molecular charge clouds (see Chapter IV). The third part depends on 2- and 3-center integrals. Because of the form of the Hamiltonian, the 3-center integrals can be reduced to 2-center integrals by means of simple linear transformations like  $x_B = x_C + R$ . (For the sake of brevity we write  $R$  instead of  $r_{BC}$ .) As pointed out above, we are going to limit ourselves to the 2 special orientations (the T and linear models), thereby effecting great simplification in the analysis of these integrals. These simplifications have already been pointed out in Section III.1, namely, all  $a_{ij} = 0$ ,  $i \neq j$ , and  $H_{ij} = 0$ ,  $i \neq j$ .

The present analysis is divided as follows: subsections 3a and 3b will deal with the  $H_{ij}^C$  part of the matrix elements for the T and linear models respectively, while subsections 4a and 4b will be concerned with the  $H_{ij}^L$  part of the matrix elements of the T and linear models. The  $H_{ij}^L$  matrix elements are presented in the form of tables. As can be seen from table III.2 through III.6, these matrix elements are dependent on a large number of overlap and two-center integrals, but because of the nature of the expansion used, no three-center or exchange integrals occur. Most of these integrals have not been evaluated before, because they arise only in this type of analysis. The evaluation of these integrals would be a major computational task, and is not carried out in this paper.

3a. T Model,  $H_{ij}^{(c)}$ . We classify the various order terms of  $H_{INT}$  up to and

including 4th order terms in Table III.1 to give perspective to the discussion for both sections 3 and 4. Thus, we can write  $H_{ij}^{(c)}$  in the following manner.

$$H_{ij}^{(c)} = \sum_{k,l,m} (2p_{A,i} | H_A^{kl} | 2p_{A,j}) (\psi_{BC} | H_B^{lm} + H_C^{lm} | \psi_{BC}). \quad \text{III.15}$$

Here  $H_B$  has the same functional dependence on  $x_B$  as  $H_C$  has on the  $x_C$  except for a possible change of sign. This can be best understood by noting that  $x_{1A} x_{AB} + x_{1A} x_{AC} = 0$ .

This expression occurs in  $\vec{r}_{1A} \cdot \vec{r}_{AB} + \vec{r}_{1A} \cdot \vec{r}_{AC}$ . The Hamiltonian  $\sum_{k,l,m} H_A^{kl} (H_B^{lm} + H_C^{lm})$  has only relatively few non-zero matrix elements of the crystal field type  $H_{ij}^{(c)}$ . The non-vanishing terms must involve only even polynomials in  $H_A$ , because they occur only in matrix elements of the form  $(2p_{Ai} | H_A^{kl} | 2p_{Aj})$ . The selection rules for the matrix elements  $(\psi_{BC} | H_B + H_C | \psi_{BC})$  are more complicated. The molecular wave functions  $\psi_{BC}$  are even functions under all reflections in planes perpendicular to coordinate axes which are centered in the molecule. To derive the necessary selection rules, the terms  $H_B$  and  $H_C$ , which are functions of  $(x_B, y_B, z_B)$ , and  $(x_C, y_C, z_C)$ , respectively, must be transformed to the "center of molecule" system. When this is done, and the inversion symmetry of the matrix elements examined, it is found that the only non-vanishing elements are the following:

TABLE III.1

Classification of Terms in  $H_{INT}$ , in Expansion in Appendix B.

$$H_{INT} = \sum_{k, \ell, m} H_A^{k\ell} (H_B^{m\ell} + H_C^{m\ell})$$

 $H_A^{k\ell}$ 
 $(H_B^{\ell m} + H_C^{\ell m})$ 

2nd Order Expansion:

linear in  $x_A$

linear in  $x_B, x_C$

3rd Order Expansion:

linear in  $x_A$

quadratic in  $x_B, x_C$

quadratic in  $x_A$

linear in  $x_B, x_C$

4th Order Expansion:

linear in  $x_A$

cubic in  $x_B, x_C$

quadratic in  $x_A$

quadratic in  $x_B, x_C$

cubic in  $x_A$

linear in  $x_B, x_C$

$$(\psi_{BC} | P_x^- | \psi_{BC}) \neq 0$$

$$(\psi_{BC} | Q_{kk}^+ | \psi_{BC}) \neq 0$$

III.16

$$(\psi_{BC} | T_{xkk}^- | \psi_{BC}) \neq 0.$$

The non-vanishing matrix elements of  $H_{ij}^{(c)}$  are, therefore, the following: (See Table B.7 for the terms in the expansion, and use the selection rules of equation III.16.)

$$H_{ij}^{(c)} = e^2 \sum_{r,k} (2p_{Ai} | r_A^2 | 2p_{Aj}) \left\{ \alpha_{1}^{rr} (\psi_{BC} | P_x^- | \psi_{BC}) + \alpha_{kk}^{rr} (\psi_{BC} | Q_{kk} | \psi_{BC}) \right\} \delta_{ij}. \quad \text{III.17}$$

No terms mixed in  $r_A s_A$  occur because they do not occur in the expansion of  $H_{\text{Total}}$  in combination with the required terms in  $H_B$  and  $H_C$ . See Table B.7. Here the  $(\psi_{BC} | Q_{kk} | \psi_{BC})$  are proportional to definite combinations of the components of the quadrupole moment of the molecule (cf. Ref. 17 pp 839, 840). This relation is striking and will be further commented upon in the next chapter.

3b. Linear Model,  $H_{ij}^{(c)}$ . The analysis is here somewhat more

involved than above, because the functional dependence of  $H_B^{ml}$  and  $H_C^{ml}$  on their respective coordinates is not the same. This implies that in general  $(\psi_{BC} | H_B^{ml} + H_C^{ml} | \psi_{BC}) \neq 0$  even if  $H_B^{ml}$  and  $H_C^{ml}$  have the same odd power dependence on their respective coordinates.

When the selection rules for the matrix elements  $(\psi_{BC}|H_B + H_C|\psi_{BC})$  are determined, it is found that the only non-zero elements are the following (P stands for either B or C):

$$(\psi_{BC}|x_B|\psi_{BC}) = \frac{1}{2} x_{BC} \neq 0$$

$$(\psi_{BC}|x_C|\psi_{BC}) = -\frac{1}{2} x_{BC} \neq 0$$

$$(\psi_{BC}|r_P^2|\psi_{BC}) \neq 0$$

$$(\psi_{BC}|x_P^3|\psi_{BC}) \neq 0$$

III.18

$$(\psi_{BC}|x_P y_P^2|\psi_{BC}) \neq 0$$

$$(\psi_{BC}|x_P z_P^2|\psi_{BC}) \neq 0.$$

Because only even powers of  $r_A$  can produce non-zero matrix elements of the form  $(2p_{Ai}|H_A|2p_{Aj})$ , which are the multipliers of the matrix elements of equation III.18, only the matrix elements of the form  $(\psi_{BC}|x_P|\psi_{BC})$  and  $(\psi_{BC}|r_P^2|\psi_{BC})$  will occur in  $H_{ij}^{(c)}$ , the crystal field part of  $H_{INT}$ .

The matrix elements of  $H_{ij}^{(c)}$  for the linear model are, therefore:

$$H_{ij}^{(c)} = e^2 \sum_{P,k,r,s} (\psi_{BC}|a_{Pk}^{rs} k_P|\psi_{BC})(2p_{A,i}|r_A s_A|2p_{A,j})$$

$$+ (\psi_{BC}|a_{Pkk}^{rs} k_P k_P|\psi_{BC})(2p_{A,i}|r_A s_A|2p_{A,j}).$$

Since there are no terms in  $H_{INT}$  of the form (cf. App. B, all such terms are multiplied by  $y_{AB}$  which = 0 in this case):

$\alpha_{P k_P r_A s_A}^{rs}$  ( $r \neq s$ ), and  $\alpha_{P k_P k_P r_A s_A}^{rs}$  ( $r \neq s$ ) then (cf. Section III.3a) we obtain:

$$H_{ij}^{(c)} = e^2 \sum_{P,k,r} [(\psi_{BC} | \alpha_{P1}^{rr} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{rr} k_P k_P | \psi_{BC})] (2p_{A,i} | r_A^2 | 2p_{A,j}) \delta_{ij} .$$

III.19

These quantities represent averages over the molecular coordinates which are not, as was true in the previous case, simple linear combinations of components of the quadrupole moment of the molecule.

4a. T Model,  $H'_{ij}$  Matrix Element. To facilitate the discussion,

we write (cf. Eq. III.10, 11, 12, 13):

$$H_{INT} = \sum_{\substack{k,l,r,s, \\ m,t}} \alpha_k^r P_k^\pm r_A + \alpha_k^{rs} P_k^\pm r_A s_A + \alpha_{kl}^r Q_{kl}^\pm r_A \\ + \alpha_k^{rst} P_k^\pm r_A s_A t_A + \alpha_{kl}^{rs} Q_{kl} r_A s_A + \alpha_{klm}^r T_{klm}^\pm r_A \quad \text{III.20}$$

A common factor  $e^2$  has been omitted. The following selection rules of 2- and 3-center integrals are used in deriving the expressions for  $H'_{ij}$  in the T model case.

$$(2p_x | \psi_{BC}) = (2p_z | \psi_{BC}) = 0 \quad \text{III.21}$$

$$(2p_y | \psi_{BC}) \neq 0 \quad \text{III.22}$$

$$(2p_{A,i} | P_k | \psi_{BC}) = \delta_{ik} (2p_{A,i} | P_k | \psi_{BC}) \quad \text{III.23}$$

Equation III.23 is to be interpreted as meaning:  $(2p_{A,i} | P_k | \psi_{BC}) = 0$ , unless  $i = k$ . Similarly, the equation below:

$$(2p_{A,i} | Q_{kl} | \psi_{BC}) = [\delta_{kl} \delta_{i2} + \delta_{i1} \delta_{k1} \delta_{l2} + \delta_{i3} \delta_{k3} \delta_{l2}] (2p_{A,i} | Q_{kl} | \psi_{BC}) \quad \text{III.24}$$

This last term vanishes for each  $i = 1, 2, \text{ or } 3$  unless the conditions on  $k$  and  $l$  given above are satisfied.

$$(2p_{A,i} | T_{klm} | \psi_{BC}) = \delta_{ik} \delta_{lm} (2p_{A,i} | T_{klm} | \psi_{BC}) \quad \text{III.25}$$

$$(2p_{A,i} | r_A | \psi_{BC}) = \delta_{ir} (2p_{A,i} | r_A | \psi_{BC}) \quad \text{III.26}$$

$$(2p_{A,i} | r_A s_A | \psi_{BC}) = [\delta_{i2} \delta_{rs} + \delta_{i1} \delta_{r1} \delta_{s2} + \delta_{i3} \delta_{r3} \delta_{s2}] (2p_{A,i} | r_A s_A | \psi_{BC}). \quad \text{III.27}$$

The same remark that was made after equation III.24 applies here too.

$$(2p_{A,i} | r_A s_A t_A | \psi_{BC}) = \delta_{ir} \delta_{st} (2p_{A,i} | r_A s_A t_A | \psi_{BC}). \quad \text{III.28}$$

The results in equations III.21 - 28 are easily derived by considering the symmetry properties of the matrix elements, particularly their behavior under reflections in planes perpendicular to the coordinate axes, with origin at the center of the molecule. The results for the elements  $H_{ij}^I$  are presented in Tables III.2 - 5. The elements  $H_{ij}^I$  ( $i \neq j$ ) vanish identically, as can be shown by use of the selection rules and the explicit expressions for  $H_{INT}^I$ . We only present the  $H_{ii}^I$  matrix elements, since it can be shown that  $H_{ij}^I = 0$ ,  $i \neq j$  in the T case (Appendix I, Reference 16

These complicated results still contain 3-center integrals.

They are presented in such a form that they do not depend on the specific form of the one-electron molecular orbital. As such, they are of general interest. We can, by means of linear transformations like  $x_B = x_C + R$ , transform these 3-center integrals into linear combinations of 2-center integrals if we substitute the specific function which stands for  $\psi_{BC}$  (cf. Equation III.1) and transform the integrals to standard form<sup>19</sup>.

TABLE III.2

T Model. Matrix Element  $H'_{11}$ .

$$\begin{aligned}
H'_{11} = e^2 & \left\{ (2p_x | \alpha_1^1 P_x | \psi_{BC}) (\psi_{BC} | x_A | 2p_x) \right. \\
& + (2p_x | \alpha_1^{21} P_x | \psi_{BC}) (\psi_{BC} | y_A x_A | 2p_x) \\
& + (2p_x | \alpha_1^{111} T_{xxx} + \alpha_1^{122} T_{xyy} + \alpha_1^{133} T_{xzz} | \psi_{BC}) (\psi_{BC} | x_A^3 | 2p_x) \\
& + (2p_x | \alpha_1^{111} P_x | \psi_{BC}) (\psi_{BC} | x_A^3 | 2p_x) \\
& + (2p_x | \alpha_1^{122} P_x | \psi_{BC}) (\psi_{BC} | x_A y_A^2 | 2p_x) \\
& + (2p_x | \alpha_1^{133} P_x | \psi_{BC}) (\psi_{BC} | x_A z_A^2 | 2p_x) \\
& \left. + \alpha_{12}^1 (2p_x | Q_{xy} | \psi_{BC}) (\psi_{BC} | x_A | 2p_x) + \alpha_{12}^{12} (2p_x | Q_{xy} | \psi_{BC}) (\psi_{BC} | x_A y_A | 2p_x) \right\} .
\end{aligned}$$

$$\alpha_1^1 = r_{AB}^{-3} - 3r_{AB}^{-5} x_{AB}^2$$

$$\alpha_1^{21} = -3r_{AB}^{-5} y_{AB} + 15r_{AB}^{-7} x_{AB}^2 y_{AB}$$

$$\alpha_{111}^1 = -(3/2)r_{AB}^{-5} + 15r_{AB}^{-7} x_{AB}^2 - (35/2)r_{AB}^{-9} x_{AB}^4$$

$$\alpha_{122}^1 = 6r_{AB}^{-5} - (105/2)r_{AB}^{-9} x_{AB}^2 y_{AB}^2$$

$$\alpha_{133}^1 = -(3/2)r_{AB}^{-5} + (15/2)r_{AB}^{-7} x_{AB}^2$$

$$\alpha_1^{111} = -(3/2)r_{AB}^{-5} + 15r_{AB}^{-7} x_{AB}^2 - (35/2)r_{AB}^{-9} x_{AB}^4$$

$$\alpha_1^{122} = (9/2)r_{AB}^{-5} - (35/2)(3x_{AB}^2 y_{AB}^2) r_{AB}^{-9}$$

$$\alpha_1^{133} = -(3/2)r_{AB}^{-5} + (15/2)r_{AB}^{-7} x_{AB}^2$$

$$\alpha_{12}^1 = -15r_{AB}^{-7} x_{AB}^2 y_{AB} + 3r_{AB}^{-5} y_{AB}$$

$$\alpha_{12}^{12} = -12r_{AB}^{-5} + 105 r_{AB}^{-9} x_{AB}^2 y_{AB}^2$$

TABLE III.3

T Model. Matrix Element  $H'_{22}$ .

$$\begin{aligned}
H'_{22} = & e^2 \left\{ (2p_y | a_2^2 P_y | \psi_{BC}) (\psi_{BC} | y_A | 2p_y) \right. \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_{11}^2 Q_{xx} + a_{22}^2 Q_{yy} + a_{33}^2 Q_{zz} | \psi_{BC}) (\psi_{BC} | y_A | 2p_y) \\
& + (2p_y | a_2^{11} P_y | \psi_{BC}) (\psi_{BC} | x_A^2 | 2p_y) + (2p_y | a_2^{22} P_y | \psi_{BC}) (\psi_{BC} | y_A^2 | 2p_y) \\
& \quad \quad \quad + (2p_y | a_2^{33} P_y | \psi_{BC}) (\psi_{BC} | z_A^2 | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_{11}^{11} Q_{xx} + a_{22}^{11} Q_{yy} + a_{33}^{11} Q_{zz} | \psi_{BC}) (\psi_{BC} | x_A^2 | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_{11}^{22} Q_{xx} + a_{22}^{22} Q_{yy} + a_{33}^{22} Q_{zz} | \psi_{BC}) (\psi_{BC} | y_A^2 | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_{11}^{33} Q_{xx} + a_{22}^{33} Q_{yy} + a_{33}^{33} Q_{zz} | \psi_{BC}) (\psi_{BC} | z_A^2 | 2p_y) \\
& + (2p_y | a_{112}^2 T_{xxy} + a_{222}^2 T_{yyy} + a_{332}^2 T_{yzz} | \psi_{BC}) (\psi_{BC} | y_A | 2p_y) \\
& + (2p_y | a_{11}^{11} Q_{xx} + a_{22}^{11} Q_{yy} + a_{33}^{11} Q_{zz} | \psi_{BC}) (\psi_{BC} | x_A^2 | 2p_y) \\
& + (2p_y | a_{11}^{22} Q_{xx} + a_{22}^{22} Q_{yy} + a_{33}^{22} Q_{zz} | \psi_{BC}) (\psi_{BC} | y_A^2 | 2p_y) \\
& + (2p_y | a_{11}^{33} Q_{xx} + a_{22}^{33} Q_{yy} + a_{33}^{33} Q_{zz} | \psi_{BC}) (\psi_{BC} | z_A^2 | 2p_y) \\
& + (2p_y | a_2^{112} P_y | \psi_{BC}) (\psi_{BC} | y_A x_A^2 | 2p_y) + (2p_y | a_2^{222} P_y | \psi_{BC}) (\psi_{BC} | y_A^3 | 2p_y) \\
& + (2p_y | a_2^{233} P_y | \psi_{BC}) (\psi_{BC} | y_A z_A^2 | 2p_y) \\
& + (2p_y | a_{11}^2 Q_{xx} + a_{22}^2 Q_{yy} + a_{33}^2 Q_{zz} | \psi_{BC}) (\psi_{BC} | y_A | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_1^{222} P_x^- | \psi_{BC}) (\psi_{BC} | y_A^3 | 2p_y) \\
& \left. + (2p_y | \psi_{BC}) (\psi_{BC} | a_1^{112} P_x^- | \psi_{BC}) (\psi_{BC} | y_A x_A^2 | 2p_y) \right\} .
\end{aligned}$$

TABLE III.3 (cont.)

$$\begin{aligned}
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_1^2 P_x^- | \psi_{BC}) (\psi_{BC} | y_A | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_1^{11} P_x^- | \psi_{BC}) (\psi_{BC} | x_A^2 | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_1^{22} P_x^- | \psi_{BC}) (\psi_{BC} | y_A^2 | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_1^{33} P_x^- | \psi_{BC}) (\psi_{BC} | z_A^2 | 2p_y) \\
& + (2p_y | \psi_{BC}) (\psi_{BC} | a_1^{233} P_x^- | \psi_{BC}) (\psi_{BC} | y_A z_A^2 | 2p_y)
\end{aligned}$$

TABLE III.4

H<sub>INT</sub> COEFFICIENTS OF H<sub>22</sub>' T MODEL.

$$\alpha_2^2 = r_{AB}^{-5} (x_{AB}^2 - 2y_{AB}^2)$$

$$\alpha_{11}^2 = (3/2) r_{AB}^{-5} y_{AB} - (15/2) r_{AB}^{-7} y_{AB} x_{AB}^2$$

$$\alpha_{22}^2 = (9/2) r_{AB}^{-5} y_{AB} - (15/2) r_{AB}^{-7} y_{AB}^3$$

$$\alpha_{33}^2 = (3/2) r_{AB}^{-5} y_{AB}$$

$$\alpha_2^{11} = -(3/2) r_{AB}^{-5} y_{AB} + (15/2) r_{AB}^{-7} x_{AB}^2 y_{AB}$$

$$\alpha_2^{22} = -(9/2) r_{AB}^{-5} y_{AB} + (15/2) r_{AB}^{-7} y_{AB}^3$$

$$\alpha_2^{33} = -(3/2) r_{AB}^{-5} y_{AB}$$

$$\alpha_{11}^{11} = (9/4) r_{AB}^{-5} - (45/2) r_{AB}^{-7} x_{AB}^2 + (105/4) r_{AB}^{-9} x_{AB}^4$$

$$\alpha_{22}^{11} = -3r_{AB}^{-5} + (105/4) r_{AB}^{-9} x_{AB}^2 y_{AB}^2$$

$$\alpha_{33}^{11} = (3/4) r_{AB}^{-5} - (15/4) x_{AB}^2 r_{AB}^{-7}$$

$$\alpha_{11}^{22} = -3 r_{AB}^{-5} + (105/4) r_{AB}^{-9} y_{AB}^2 x_{AB}^2$$

$$\alpha_{22}^{22} = (9/4) r_{AB}^{-5} - (45/2) r_{AB}^{-7} y_{AB}^2 + (105/4) r_{AB}^{-9} y_{AB}^4$$

$$\alpha_{33}^{22} = (3/4) r_{AB}^{-5} - (15/4) r_{AB}^{-7} y_{AB}^2$$

$$\alpha_{11}^{33} = (3/4) r_{AB}^{-5} - (15/4) r_{AB}^{-7} x_{AB}^2$$

TABLE III.4 (cont.)

$$\alpha_{22}^{33} = (3/4) r_{AB}^{-5} - (15/4) r_{AB}^{-7} y_{AB}^2$$

$$\alpha_{33}^{33} = (9/4) r_{AB}^{-5}$$

$$\alpha_{112}^2 = 6r_{AB}^{-5} - (105/2) r_{AB}^{-9} x_{AB}^2 y_{AB}^2$$

$$\alpha_{222}^2 = -(3/2) r_{AB}^{-5} + 15 r_{AB}^{-7} y_{AB}^2 - (35/2) r_{AB}^{-9} y_{AB}^4$$

$$\alpha_{233}^2 = -(3/2) r_{AB}^{-5} + (15/2) r_{AB}^{-7} y_{AB}^2$$

$$\alpha_2^{112} = 6 r_{AB}^{-5} - (105/2) r_{AB}^{-9} x_{AB}^2 y_{AB}^2$$

$$\alpha_2^{222} = -(3/2) r_{AB}^{-5} + 15 r_{AB}^{-7} y_{AB}^2 - (35/2) r_{AB}^{-9} y_{AB}^4$$

$$\alpha_2^{233} = (3/2) r_{AB}^{-5} + (15/2) r_{AB}^{-7} y_{AB}^2$$

$$\alpha_1^{222} = (15/2) r_{AB}^{-7} x_{AB} y_{AB}^2 - (35/2) r_{AB}^{-9} x_{AB} y_{AB}^3$$

$$\alpha_1^{112} = (15/2) r_{AB}^{-7} 3x_{AB} y_{AB}^2 - (35/2) 3r_{AB}^{-9} x_{AB} y_{AB}^3$$

$$\alpha_1^2 = -3 r_{AB}^{-5} x_{AB} y_{AB}$$

$$\alpha_1^{11} = -(3/2) r_{AB}^{-5} 3x_{AB} + (15/2) r_{AB}^{-7} x_{AB}^3$$

$$\alpha_1^{22} = (15/2) r_{AB}^{-7} y_{AB}^2 x_{AB}$$

$$\alpha_1^{33} = -(3/2) r_{AB}^{-5} x_{AB}$$

$$\alpha_1^{233} = (15/2) r_{AB}^{-7} x_{AB} y_{AB}$$

TABLE III.5

 $H'_{33}$  DEPENDENCE ON 2- AND 3-CENTER INTEGRALS. T MODEL.

$$\begin{aligned}
 H'_{33} = e^2 \{ & (2p_z | \alpha_3^3 P_z | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
 & + (2p_z | \alpha_3^3 P_z | \Psi_{BC}) (\Psi_{BC} | y_A z_A | 2p_z) \\
 & + (2p_z | \alpha_{113}^3 T_{xxz} | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
 & + (2p_z | \alpha_{213}^3 T_{yyz} | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
 & + (2p_z | \alpha_{333}^3 T_{zzz} | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
 & + (2p_z | \alpha_3^{113} P_z | \Psi_{BC}) (\Psi_{BC} | z_A x_A^2 | 2p_z) \\
 & + (2p_z | \alpha_3^{223} P_z | \Psi_{BC}) (\Psi_{BC} | z_A y_A^2 | 2p_z) \\
 & + (2p_z | \alpha_3^{333} P_z | \Psi_{BC}) (\Psi_{BC} | z_A^3 | 2p_z) \\
 & + (2p_z | \alpha_{23}^3 Q_{yz} | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
 & + (2p_z | \alpha_{23}^3 Q_{yz} | \Psi_{BC}) (\Psi_{BC} | y_A z_A | 2p_z) \} .
 \end{aligned}$$

TABLE III.5 (cont.)

HINT COEFFICIENTS OF  $H_{33}$ . T MODEL.

$$\alpha_3^3 = r_{AB}^{-3}$$

$$\alpha_3^{23} = -3r_{AB}^{-5}y_{AB}$$

$$\alpha_{113}^3 = -(3/2)r_{AB}^{-5} + (15/2)r_{AB}^{-7}x_{AB}^2$$

$$\alpha_{223}^3 = -(3/2)r_{AB}^{-5} + (15/2)r_{AB}^{-7}y_{AB}^2$$

$$\alpha_{333}^3 = -(3/2)r_{AB}^{-5}$$

$$\alpha_3^{113} = -(3/2)r_{AB}^{-5} + (15/2)r_{AB}^{-7}x_{AB}^2$$

$$\alpha_3^{223} = -(3/2)r_{AB}^{-5} + (15/2)r_{AB}^{-7}y_{AB}^2$$

$$\alpha_3^{333} = -(3/2)r_{AB}^{-5}$$

$$\alpha_{23}^3 = 3r_{AB}^{-5}y_{AB}$$

$$\alpha_{23}^{23} = 3r_{AB}^{-5} - 15r_{AB}^{-7}y_{AB}^2$$

Thus the only integrals that must be evaluated are relatively easily evaluated double integrals. Then it is just a matter of using linear substitutions to obtain the final numerical values of  $H'_{ij}$ .

4b. Linear Model,  $H'_{ij}$  Matrix Elements. The analysis proceeds in similar fashion to the one given in the previous section. To simplify matters, the interaction Hamiltonian is repeated in the short notation (cf. Equation III.14).

$$\begin{aligned}
 H_{\text{INT}} = & \sum_{P,k,r} \alpha_{Pk}^r k_P r_A \\
 & + \sum_{P,k,l,r,s} \left\{ \alpha_{Pkl}^r k_P l_P r_A + \alpha_{Pk}^{rs} k_P r_A s_A \right\} \\
 & + \sum_{P,k,l,m,r,s,t} \left\{ \alpha_{Pklm}^r k_P l_P^m r_A + \alpha_{Pkl}^{rs} k_P l_P r_A s_A \right. \\
 & \qquad \qquad \qquad \left. + \alpha_{Pk}^{rst} k_P r_A s_A t_A \right\}.
 \end{aligned}$$

III.1.

A common factor  $e^2$  has been omitted.

Before we present the  $H'_{ij}$  matrix elements for the linear case, we list some of the symmetry properties of the many-center integrals which occur. These properties are readily established in the same way as equations III.21 - 28.

$$(2p_x | \psi_{BC}) \neq 0 \quad \text{III.29}$$

$$(2p_y | \psi_{BC}) = (2p_z | \psi_{BC}) = 0 \quad \text{III.30}$$

$$(2p_{A,i} | k_P | \psi_{BC}) = \delta_{ik} (2p_{A,i} | k_P | \psi_{BC}) \quad \text{III.31}$$

$$(2p_{A,i} | k_P \ell_P | \psi_{BC}) = \quad \text{III.32}$$

$$(\delta_{i1} \delta_{k\ell} + \delta_{i2} \delta_{k2} \delta_{\ell 1} + \delta_{i3} \delta_{k3} \delta_{\ell 1}) (2p_{A,i} | k_P \ell_P | \psi_{BC}).$$

This last expression vanishes for  $i = 1, 2,$  or  $3$  unless the conditions on  $k$  and  $\ell$  are satisfied.

$$(2p_{A,i} | k_P \ell_P m_P | \psi_{BC}) = \delta_{ik} \delta_{\ell m} (2p_{A,i} | k_P \ell_P m_P | \psi_{BC}) \quad \text{III.33}$$

$$(2p_{A,i} | r_A | \psi_{BC}) = \delta_{ir} (2p_{A,i} | r_A | \psi_{BC}) \quad \text{III.34}$$

$$(2p_{A,i} | r_A s_A | \psi_{BC}) = \quad \text{III.35}$$

$$[\delta_{i1} \delta_{rs} + \delta_{i2} \delta_{r2} \delta_{s1} + \delta_{i3} \delta_{r3} \delta_{s1}] (2p_{A,i} | r_A s_A | \psi_{BC}).$$

The same remark applies here as the one made after Equation III.32.

$$(2p_{A,i} | r_A s_A t_A | \psi_{BC}) = \delta_{ir} \delta_{st} (2p_{A,i} | r_A s_A t_A | \psi_{BC}). \quad \text{III.36}$$

Similar selection rules can be derived for integrals over  $\psi_{BC}$  only.

With these properties at our disposal, it is easy to derive the matrix elements  $H'_{ii}$ . The  $H'_{ij}$ , just as in the T model, are identically zero. The non-vanishing matrix elements are presented in Table III.6. The coefficients dependent on the geometry of the problem are somewhat more complicated than those of the T model, due to the fact that in general  $a_{B\dots} \neq a_{C\dots}$ .

TABLE III.6

## LINEAR MODEL MATRIX ELEMENTS.

$$\begin{aligned}
H'_{11} = & e^2 \sum_P (2p_x | \alpha_{p1}^1 x_p | \psi_{BC}) (\psi_{BC} | x_A | 2p_x) \\
& + (2p_x | \psi_{BC}) (\psi_{BC} | \alpha_{p1}^1 x_p | \psi_{BC}) (\psi_{BC} | x_A | 2p_x) \\
& + (2p_x | \psi_{BC}) (\psi_{BC} | \alpha_{p11}^1 x_p x_p + \alpha_{p22}^1 y_p y_p + \alpha_{p33}^1 z_p z_p | \psi_{BC}) (\psi_{BC} | x_A | 2p_x) \\
& + (2p_x | \alpha_{p11}^1 x_p x_p + \alpha_{p22}^1 y_p y_p + \alpha_{p33}^1 z_p z_p | \psi_{BC}) (\psi_{BC} | x_A | 2p_x) \\
& + (2p_x | \alpha_{p1}^{11} x_p | \psi_{BC}) (\psi_{BC} | x_A^2 | 2p_x) \\
& + (2p_x | \alpha_{p1}^{33} x_p | \psi_{BC}) (\psi_{BC} | z_A^2 | 2p_x) \\
& + (2p_x | \psi_{BC}) (\psi_{BC} | \alpha_{p1}^{11} x_p | \psi_{BC}) (\psi_{BC} | x_A^2 | 2p_x) \\
& + (2p_x | \psi_{BC}) (\psi_{BC} | \alpha_{p1}^{33} x_p | \psi_{BC}) (\psi_{BC} | z_A^2 | 2p_x)
\end{aligned}$$

TABLE III.6 (cont.)

$$\begin{aligned}
& + (2P_X | \Psi_{BC}) (\Psi_{BC} | \alpha_{P11}'' x_P x_P + \alpha_{P22}'' y_P y_P + \alpha_{P33}'' z_P z_P | \Psi_{BC}) (\Psi_{BC} | x_A x_A | 2P_X) \\
& + (2P_X | \Psi_{BC}) (\Psi_{BC} | \alpha_{P11}^{22} x_P x_P + \alpha_{P22}^{22} y_P y_P + \alpha_{P33}^{22} z_P z_P | \Psi_{BC}) (\Psi_{BC} | y_A y_A | 2P_X) \\
& + (2P_X | \Psi_{BC}) (\Psi_{BC} | \alpha_{P11}^{33} x_P x_P + \alpha_{P22}^{33} y_P y_P + \alpha_{P33}^{33} z_P z_P | \Psi_{BC}) (\Psi_{BC} | z_A z_A | 2P_X) \\
& + (2P_X | \alpha_{P111}' x_P x_P x_P + \alpha_{P122}' x_P y_P y_P + \alpha_{P133}' x_P z_P z_P | \Psi_{BC}) (\Psi_{BC} | x_A | 2P_X) \\
& + (2P_X | \alpha_{P11}'' x_P x_P + \alpha_{P22}'' y_P y_P + \alpha_{P33}'' z_P z_P | \Psi_{BC}) (\Psi_{BC} | x_A x_A | 2P_X) \\
& + (2P_X | \alpha_{P11}^{22} x_P x_P + \alpha_{P22}^{22} y_P y_P + \alpha_{P33}^{22} z_P z_P | \Psi_{BC}) (\Psi_{BC} | y_A y_A | 2P_X) \\
& + (2P_X | \alpha_{P11}^{33} x_P x_P + \alpha_{P22}^{33} y_P y_P + \alpha_{P33}^{33} z_P z_P | \Psi_{BC}) (\Psi_{BC} | z_A z_A | 2P_X) \\
& + (2P_X | (\alpha_{P1}''') x_P | \Psi_{BC}) (\Psi_{BC} | x_A x_A x_A | 2P_X) \\
& + (2P_X | \alpha_{P1}^{122} x_P | \Psi_{BC}) (\Psi_{BC} | x_A y_A y_A | 2P_X) \\
& + (2P_X | \alpha_{P1}^{133} x_P | \Psi_{BC}) (\Psi_{BC} | x_A z_A z_A | 2P_X) \\
& + (2P_X | \Psi_{BC}) (\Psi_{BC} | \alpha_{P111}^1 x_P^3 + \alpha_{P122}^1 x_P y_P^2 + \alpha_{P133}^1 x_P z_P^2 | \Psi_{BC}) (\Psi_{BC} | x_A | 2P_X) \\
& + (2P_X | \Psi_{BC}) (\Psi_{BC} | \alpha_{P1}^{111} x_P | \Psi_{BC}) (\Psi_{BC} | x_A^3 | 2P_X) + (2P_X | \Psi_{BC}) (\Psi_{BC} | \alpha_{P1}^{122} x_P | \Psi_{BC}) (\Psi_{BC} | x_A y_A^2 | 2P_X) \\
& + (2P_X | \Psi_{BC}) (\Psi_{BC} | \alpha_{P1}^{133} x_P | \Psi_{BC}) (\Psi_{BC} | x_A z_A^2 | 2P_X)
\end{aligned}$$

TABLE III.6 (cont.)

COEFFICIENTS IN  $H'_{11}$ .

$$\alpha'_{B1} = -2x_{AB}^2 r_{AB}^{-5} = -2x_{AB}^{-3}$$

$$\alpha'''_{B1} = -4x_{AB}^{-5}$$

$$\alpha'_{B11} = -3x_{AB}^{-4}$$

$$\alpha^{122}_{B1} = 6x_{AB}^{-5}$$

$$\alpha'_{B22} = (3/2)x_{AB}^{-4}$$

$$\alpha^{133}_{B1} = 6x_{AB}^{-5}$$

$$\alpha'_{B33} = (3/2)x_{AB}^{-4}$$

$$\alpha'_{C1} = -2x_{AC}^{-3}$$

$$\alpha''_{B11} = 6x_{AB}^{-5}$$

$$\alpha'_{C11} = +3x_{AC}^{-4}$$

$$\alpha''_{B22} = -3x_{AB}^{-5}$$

$$\alpha'_{C22} = -(3/2)x_{AC}^{-4}$$

$$\alpha''_{B33} = -3x_{AB}^{-5}$$

$$\alpha'_{C33} = -(3/2)x_{AC}^{-4}$$

$$\alpha^{22}_{B11} = -3x_{AB}^{-5}$$

$$\alpha''_{C11} = 6x_{AC}^{-5}$$

$$\alpha^{32}_{B22} = (9/4)x_{AB}^{-5}$$

$$\alpha''_{C22} = -3x_{AC}^{-5}$$

$$\alpha^{22}_{B33} = (3/4)x_{AB}^{-5}$$

$$\alpha''_{C33} = -3x_{AC}^{-5}$$

$$\alpha^{33}_{B11} = -3x_{AB}^{-5}$$

$$\alpha^{22}_{C11} = -3x_{AC}^{-5}$$

$$\alpha^{33}_{B22} = (3/4)x_{AB}^{-5}$$

$$\alpha^{22}_{C22} = (9/4)x_{AC}^{-5}$$

$$\alpha^{33}_{B33} = (9/4)x_{AB}^{-5}$$

$$\alpha^{22}_{C33} = (3/4)x_{AC}^{-5}$$

$$\alpha'_{B111} = -4x_{AB}^{-5}$$

$$\alpha^{33}_{C11} = -3x_{AC}^{-5}$$

$$\alpha'_{B122} = +6x_{AB}^{-5}$$

$$\alpha^{33}_{C22} = (3/4)x_{AC}^{-5}$$

$$\alpha'_{B133} = +6x_{AB}^{-5}$$

$$\alpha^{33}_{C33} = (9/4)x_{AC}^{-5}$$

TABLE III.6 (cont.)

$$\alpha_{C111}^1 = -4 x_{AC}^{-5}$$

$$\alpha_{C122}^1 = +6 x_{AC}^{-5}$$

$$\alpha_{C133}^1 = +6 x_{AC}^{-5}$$

$$\alpha_{C1}^{111} = -4 x_{AC}^{-5}$$

$$\alpha_{C1}^{122} = 6 x_{AC}^{-5}$$

$$\alpha_{C1}^{133} = 6 x_{AC}^{-5}$$

$$\alpha_{B1}^{11} = 3 x_{AB}^{-4}$$

$$\alpha_{B1}^{33} = -(3/2) x_{AB}^{-4}$$

$$\alpha_{C1}^{11} = -3 x_{AC}^{-4}$$

$$\alpha_{C1}^{33} = +(3/2) x_{AC}^{-4}$$

TABLE III.6 (cont.)

LINEAR MODEL  $H'_{22}$ .

$$\begin{aligned}
 H'_{22} = & e^2 \sum_P \left[ (2P_Y | \alpha_{P2}^2 y_P | \Psi_{BC}) (\Psi_{BC} | y_A | 2P_Y) \right. \\
 & + (2P_Y | \alpha_{P12}^2 y_P x_P | \Psi_{BC}) (\Psi_{BC} | y_A | 2P_Y) \\
 & + (2P_Y | \alpha_{P2}^{12} y_P | \Psi_{BC}) (\Psi_{BC} | x_A y_A | 2P_Y) \\
 & + (2P_Y | \alpha_{P112}^2 y_P x_P x_P + \alpha_{P222}^2 y_P y_P y_P + \alpha_{P233}^2 y_P z_P z_P | \Psi_{BC}) (\Psi_{BC} | y_A | 2P_Y) \\
 & + (2P_Y | \alpha_{P21}^{21} x_P y_P | \Psi_{BC}) (\Psi_{BC} | x_A y_A | 2P_Y) \\
 & + (2P_Y | \alpha_{P2}^{112} y_P | \Psi_{BC}) (\Psi_{BC} | y_A x_A x_A | 2P_Y) \\
 & + (2P_Y | \alpha_{P2}^{222} y_P | \Psi_{BC}) (\Psi_{BC} | y_A y_A y_A | 2P_Y) \\
 & \left. + (2P_Y | \alpha_{P2}^{233} | y_P | \Psi_{BC}) (\Psi_{BC} | y_A z_A z_A | 2P_Y) \right]
 \end{aligned}$$

$$\alpha_{B2}^2 = x_{AB}^{-3}$$

$$\alpha_{C2}^2 = x_{AC}^{-3}$$

$$\alpha_{B21}^2 = 3x_{AB}^{-4}$$

$$\alpha_{C21}^2 = -3x_{AC}^{-4}$$

$$\alpha_{B2}^{12} = -3x_{AB}^{-4}$$

$$\alpha_{C2}^{12} = +3x_{AC}^{-4}$$

$$\alpha_{B211}^2 = 6x_{AB}^{-5}$$

$$\alpha_{C211}^2 = 6x_{AC}^{-5}$$

$$\alpha_{B222}^2 = -(3/2)x_{AB}^{-5}$$

$$\alpha_{C222}^2 = -(3/2)x_{AC}^{-5}$$

$$\alpha_{B233}^2 = -(3/2)x_{AB}^{-5}$$

$$\alpha_{C233}^2 = -(3/2)x_{AC}^{-5}$$

$$\alpha_{B21}^{21} = -12x_{AB}^{-5}$$

$$\alpha_{C21}^{21} = -12x_{AC}^{-5}$$

$$\alpha_{B2}^{211} = 6x_{AB}^{-5}$$

$$\alpha_{C2}^{211} = 6x_{AC}^{-5}$$

$$\alpha_{B2}^{222} = -(3/2)x_{AB}^{-5}$$

$$\alpha_{C2}^{222} = -(3/2)x_{AC}^{-5}$$

$$\alpha_{B2}^{233} = -(3/2)x_{AB}^{-5}$$

$$\alpha_{C2}^{233} = -(3/2)x_{AC}^{-5}$$

TABLE III.6 (cont.)

 $H_{33}$ , LINEAR MODEL.

$$\begin{aligned}
e \sum_P \left[ H_{33}^1 = \right. & (2p_z | \alpha_{p3}^3 z_p | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
& + (2p_x | \alpha_{31}^3 z_p x_p | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
& + (2p_z | \alpha_{p3}^{13} z_p | \Psi_{BC}) (\Psi_{BC} | x_A z_A | 2p_z) \\
& + (2p_z | \alpha_{113}^3 z_p x_p x_p + \alpha_{p333}^3 z_p z_p z_p + \alpha_{223}^3 z_p y_p y_p | \Psi_{BC}) (\Psi_{BC} | z_A | 2p_z) \\
& + (2p_z | \alpha_{p13}^{13} x_p z_p | \Psi_{BC}) (\Psi_{BC} | x_A z_A | 2p_z) \\
& + (2p_z | \alpha_{p3}^{113} z_p | \Psi_{BC}) (\Psi_{BC} | x_A x_A z_A | 2p_z) \\
& + (2p_z | \alpha_{p3}^{223} z_p | \Psi_{BC}) (\Psi_{BC} | y_A y_A z_A | 2p_z) \\
& \left. + (2p_z | \alpha_{p3}^{333} z_p | \Psi_{BC}) (\Psi_{BC} | z_A z_A z_A | 2p_z) \right]
\end{aligned}$$

$$\alpha_{B3}^3 = x_{AB}^{-3}$$

$$\alpha_{B31}^3 = 3x_{AB}^{-4}$$

$$\alpha_{B3}^{13} = -3x_{AB}^{-4}$$

$$\alpha_{B113}^3 = 6x_{AB}^{-5}$$

$$\alpha_{B333}^3 = -(3/2) x_{AB}^{-5}$$

$$\alpha_{B223}^3 = -(3/2) x_{AB}^{-5}$$

$$\alpha_{B31}^{31} = -12x_{AB}^{-5}$$

$$\alpha_{B3}^{113} = 6x_{AB}^{-5}$$

$$\alpha_{B3}^{333} = -(3/2) x_{AB}^{-5}$$

$$\alpha_{B3}^{223} = -(3/2) x_{AB}^{-5}$$

To obtain  $\alpha_{BA}^{3-}$  replace  
 subscript B by subscript  
 C. (e.g.  $\alpha_{B3}^3 = x_{AC}^{-3}$ )  
 except that

$$\alpha_{C31}^3 = -3 x_{AB}^{-4}$$

$$\alpha_{C3}^{13} = +3 x_{AB}^{-4}$$

## CHAPTER IV

## COMPARISON OF CRYSTAL FIELD SPLITTING WITH THIS THEORY

In this chapter we compare critically the application of both crystal field theory and expanded Hamiltonian molecular orbital (EHSAMO) theory to the interaction between the  $H_2$  molecule and the H atom. The comparison will consist of comparing the splittings obtained by means of both methods in the two special cases, the linear and T models. Sections 1 and 2 treat the linear case by means of crystal field theory and EHSAMO theory respectively, while sections 3 and 4 treat the T model.

1. Linear Model, Crystal Field Calculation. We apply crystal field theory in the usual way. We replace the  $H_2$  molecule by a linear point charge quadrupole and compute the splitting of the 2p state of a hydrogen atom due to this quadrupole field. We expand the quadrupole potential about the nucleus of the atom, to obtain a series expansion of the form

$$V = C + a_1 x_A + A_{11} x_A^2 + A_{22} y_A^2 + A_{33} z_A^2 . \quad \text{IV.1}$$

The  $x_A$  are electron coordinates with respect to the nucleus of the H atom, i.e. center A. The meaning of the parameters is<sup>15</sup>:

$$C = \epsilon \left( \frac{1}{x_0 + a} - \frac{2}{x_0} + \frac{1}{x_0 - a} \right)$$

$$\alpha = -\epsilon \left[ \frac{1}{(x_0 + a)^2} - \frac{2}{x_0^2} + \frac{1}{(x_0 - a)^2} \right]$$

$$A_{11} = \epsilon \left[ \frac{1}{(x_0 + a)^3} - \frac{2}{x_0^3} + \frac{1}{(x_0 - a)^3} \right]$$

IV.2

$$A_{22} = A_{33} = -\left(\frac{1}{2}\right) \epsilon \left[ \frac{1}{(x_0 + a)^3} - \frac{2}{x_0^3} + \frac{1}{(x_0 - a)^3} \right]$$

$$A_{12} = A_{13} = A_{23} = 0.$$

Here the coordinates of the H atom in the center of molecule system are  $x_0, y_0, z_0$ , with  $y_0 = z_0 = 0$ . The coordinates of the nuclei of the molecule, in the same system, are  $x_0 = -a$  for nucleus B and

$x_0 = a$  for nucleus C. The point charge distribution is the following: a charge of  $\epsilon$  on each nucleus, and one of  $-2\epsilon$  at the origin.  $\epsilon$  is adjusted so as to make the quadrupole moment of the charge distribution equal to the observed value of the quadrupole moment for the molecule.

We calculate the eigenvalues of the Hamiltonian

$$H = eV.$$

IV.3

We take as our basis the three atomic functions:  $2p_x, 2p_y$  and  $2p_z$ .

H is diagonal in this basis. The matrix H has the following form:

|        | $2p_x$   | $2p_y$   | $2p_z$   |
|--------|----------|----------|----------|
| $2p_x$ | $H_{11}$ | 0        | 0        |
| $2p_y$ | 0        | $H_{22}$ | 0        |
| $2p_z$ | 0        | 0        | $H_{33}$ |

Obviously,  $H_{22} = H_{33}$ , and the three eigenvalues are

$$H_{11}, \quad H_{22}, \quad \text{and} \quad H_{33}.$$

As is well known, we obtain 2 levels, one doubly degenerate and one non-degenerate level. We exhibit them here explicitly so as to make the comparisons with the results of Chapter III, in terms of the parameters  $C$ ,  $\alpha_1$ ,  $A_{11}$ , and  $A_{22}$ .

The matrix elements are:

$$\begin{aligned}
 H_{11} &= eA_{11} \int x_A^2 (2p_x)^2 d\tau + eA_{22} \left[ \int y_A^2 (2p_x)^2 d\tau + \int z_A^2 (2p_x)^2 d\tau \right] \\
 H_{22} &= eA_{11} \int x_A^2 (2p_y)^2 d\tau + eA_{22} \left[ \int y_A^2 (2p_y)^2 d\tau + \int z_A^2 (2p_y)^2 d\tau \right] \\
 H_{33} &= eA_{11} \int x_A^2 (2p_z)^2 d\tau + eA_{22} \left[ \int y_A^2 (2p_z)^2 d\tau + \int z_A^2 (2p_z)^2 d\tau \right].
 \end{aligned}
 \tag{IV.4}$$

Let the integral  $\int x_A^2 (2p_y)^2 d\tau$  be denoted by  $I_{xy}$ , etc. Symmetry provides the following identities for the integrals:

$$\begin{aligned}
 I_{ij} &= I_{ji} \\
 I_{xy} &= I_{xz} = I_{yz} \\
 I_{xx} &= I_{yy} = I_{zz}
 \end{aligned}
 \tag{IV.5}$$

and an elementary calculation shows that  $I_{xx} = 3I_{xy}$ . Using these results we obtain:

$$\begin{aligned}
 H_{11} &= 2A_{11} I_{xy} e \\
 H_{22} = H_{33} &= -A_{11} I_{xy} e.
 \end{aligned}
 \tag{IV.6}$$

The splitting is then:

$$H_{11} - H_{22} = 2I_{xy} (A_{11} - A_{22})e = 3A_{11} I_{xy} e.
 \tag{IV.7}$$

The crystal field splitting has the usual two factors: A factor which depends on the geometry of the problem and on the details of the charge distributions of the neighbors of the reference species, in this case  $A_{11}$ , and another factor, which is essentially an average of a polynomial of electron coordinates averaged over the wave functions of the reference species, in this case  $I_{xy}$ .

## 2. Linear Model, Expanded Hamiltonian Molecular Orbital Treatment.

Since  $H_{ij} = 0$ ,  $i \neq j$ , the 3 new levels arising from the original degenerate  $2p$  state under the presence of the electrostatic  $H_{INT}$  are given by  $H_{11}$ ,  $H_{22}$ , and  $H_{33}$  respectively. More explicitly, they are (Equation III.6 and III.19 and Table III.1):

$$H_{11} = E_H + E_M + N_x^2 e^2 \sum_{P,k,r} [(\psi_{BC} | \alpha_{P1}^{rr} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{rr} k_P^2 | \psi_{BC})] (2p_x | r_A^2 | 2p_x) - \frac{1}{2} N_x^2 H'_{11}$$

$$H_{22} = E_H + E_M + N_y^2 e^2 \sum_{P,k,r} [(\psi_{BC} | \alpha_{P1}^{rr} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{rr} k_P^2 | \psi_{BC})] (2p_y | r_A^2 | 2p_y) - \frac{1}{2} N_y^2 H'_{22}$$

$$H_{33} = E_H + E_M + N_z^2 e^2 \sum_{P,k,r} [(\psi_{BC} | \alpha_{P1}^{rr} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{rr} k_P^2 | \psi_{BC})] (2p_z | r_A^2 | 2p_z) - \frac{1}{2} N_z^2 H'_{33}$$

If we write out these matrix elements in a more explicit way the relationships with crystal field theory matrix elements can be brought out more clearly. Thus,

$$\begin{aligned}
 H_{11} = & E_H + E_M + e^2 \sum_{P,k} \left[ (\psi_{BC} | \alpha_{P1}^{11} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{11} k_P^2 | \psi_{BC}) \right] (2p_x | x_A^2 | 2p_x) N_x^2 \\
 & + \left[ (\psi_{BC} | \alpha_{P1}^{22} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{22} k_P^2 | \psi_{BC}) \right] (2p_x | y_A^2 | 2p_x) N_x^2 \\
 & + \left[ (\psi_{BC} | \alpha_{P1}^{33} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{33} k_P^2 | \psi_{BC}) \right] (2p_x | z_A^2 | 2p_x) N_x^2 \\
 & - \frac{1}{2} N_x^2 H_{11}' .
 \end{aligned}$$

Let us for convenience denote  $e \sum_{P,k} \left[ (\psi_{BC} | \alpha_{P1}^{rr} x_P | \psi_{BC}) + (\psi_{BC} | \alpha_{Pkk}^{rr} k_P^2 | \psi_{BC}) \right]$  by  $A'_{rr}$ . From the form of the electrostatic coefficients (cf. section IV.1) it is clear that  $A'_{22} = A'_{33}$ . Thus, we obtain:

$$H_{11} = E_H + E_M + eN_x^2 \left[ A'_{11} (2p_x | x_A^2 | 2p_x) + A'_{22} (2p_x | y_A^2 | 2p_x) + A'_{33} (2p_x | z_A^2 | 2p_x) \right] - \frac{1}{2} N_x^2 H_{11}'$$

$$H_{22} = E_H + E_M + eN_y^2 \left[ A'_{11} (2p_y | x_A^2 | 2p_y) + A'_{22} (2p_y | y_A^2 | 2p_y) + A'_{33} (2p_x | z_A^2 | 2p_y) \right] - \frac{1}{2} N_y^2 H_{22}'$$

$$H_{33} = E_H + E_M + eN_z^2 \left[ A'_{11} (2p_z | x_A^2 | 2p_z) + A'_{22} (2p_z | y_A^2 | 2p_z) + A'_{33} (2p_z | z_A^2 | 2p_z) \right] - \frac{1}{2} N_z^2 H_{33}'$$

Using the properties of the integrals  $(2p_s | r_A^2 | 2p_s) = I_{rs}$  of equations IV.5, we can now simplify the expression for the energy levels of the atom in the field of the molecule.

$$H_{11} = E_H + E_M + e(3A'_{11} I_{xy} + A'_{22} I_{xy} + A'_{33} I_{xy}) N_x^2 - \frac{1}{2} N_x^2 H'_{11}$$

$$H_{22} = E_H + E_M + e(A'_{11} I_{xy} + 3A'_{22} I_{xy} + A'_{33} I_{xy}) N_y^2 - \frac{1}{2} N_y^2 H'_{22} \quad \text{IV.9}$$

$$H_{33} = E_H + E_M + e(A'_{11} I_{xy} + A'_{22} I_{xy} + 3A'_{33} I_{xy}) N_z^2 - \frac{1}{2} N_z^2 H'_{33} .$$

$N_x^2$ , we recall, is equal to  $[1 - (2p_x | \psi_{BC})^2]^{-1}$ , while  $N_y^2 = N_z^2 = 1$

in this case (App. D). It is convenient to write

$$N_x^2 = 1 + \frac{(2p_x | \psi_{BC})^2}{1 - (2p_x | \psi_{BC})^2} = 1 + \frac{a_{11}^2}{1 - a_{11}^2} . \quad \text{There are here 2 degenerate}$$

levels just as in the previous section, and the splitting is given

as follows:

$$H_{11} - H_{22} = 2I_{xy} e(A'_{11} - A'_{22}) + \left( \frac{a_{11}^2}{1 - a_{11}^2} \right) I_{xy} e(3A'_{11} + 2A'_{22}) - \frac{1}{2} N_x^2 (H'_{11} - H'_{22}) . \quad \text{IV.10}$$

Three important terms are present in the splitting as it is obtained by the EH-SA-MO technique. The first term is analogous to the expression (IV.7) obtained in the previous section. The contribution from the first term to the splitting is proportional to  $A'_{11} - A'_{22}$ , which is analogous to  $A_{11} - A_{22}$ . While the  $A_{11}$  were proportional to the quadrupole moment of the molecule, the

$A'_{ii}$  are proportional to quantities which involve constants and the quadrupole moment of the molecule. The second term, although it contains the same parameters as the first term, has a different dependence on them. Also it contains a factor which is strongly dependent on the overlap between the charge distributions of the molecule and the atom. This factor  $\frac{a_{11}^2}{1 - a_{11}^2}$  is plotted in figure 2

as a function of  $(2p_x|\psi_{BC})$ . The approximate meaning of this is as follows: When  $r_{AB} = 2.5 \text{ \AA}$ ,  $(2p_x|1s_B) = 0.4$ . Using  $(2p_x|1s_B)$  as an estimate for  $(2p_x|\psi_{BC})$ , for purposes of illustration, we obtain  $(2p_x|\psi_{BC})^2 [1 - (2p_x|\psi_{BC})^2]^{-1} \approx 0.2$ , which is quite appreciable. For the purposes of the analysis given here this rough estimate is indicative of the relative importance of these terms. The third term contains a variety of many-center integrals which have no analog in the results obtained by means of ordinary crystal field theory. No analytical simplification results when the term  $H'_{11} - H'_{22}$  is analyzed as one, since most of the integrals occurring in  $H'_{11}$  are different from the ones appearing in  $H'_{22}$ .

3. The T Model, Crystal Field Calculation. As in section IV.1, we present the results of crystal field theory methods to determine the removal of degeneracy of the levels, so as to provide a basis for comparison in the next section. The interaction Hamiltonian is again written as follows:

$$V = C + \sum_k \alpha_k k_A + \sum A_{rs} r_A s_A . \quad \text{IV.11}$$

The  $k_A$  are electronic coordinates with respect to center A. The meaning of the parameters<sup>15</sup> is given below:

$$C = \sum_i \epsilon_i / d_i \quad \alpha_1 = 0 \quad \alpha_2 = 2y_0 \epsilon \left[ \frac{1}{(a^2 + y_0^2)^{3/2}} - \frac{1}{y_0^3} \right]$$

$$A_{11} = \epsilon \left\{ \frac{3a^2}{(a^2 + y_0^2)^{5/2}} - \left[ \frac{1}{(a^2 + y_0^2)^{3/2}} - \frac{1}{y_0^3} \right] \right\}$$

$$A_{22} = \epsilon \left\{ 3 y_0^2 \left[ \frac{1}{(a^2 + y_0^2)^{5/2}} - \frac{1}{y_0^5} \right] - \left[ \frac{1}{(a^2 + y_0^2)^{3/2}} - \frac{1}{y_0^3} \right] \right\} \quad \text{IV.12}$$

$$A_{33} = -\epsilon \left[ \frac{1}{(a^2 + y_0^3)^{3/2}} - \frac{1}{y_0^3} \right]$$

$$A_{12} = A_{23} = A_{13} = 0.$$

We write down the matrix for  $H = eV$ , remembering  $H_{ij} = 0$  for  $i \neq j$ , because  $A_{ij} = 0$  for  $i \neq j$ .

The Hamiltonian  $H = eV$  has the following non-zero matrix elements (using the notation of the previous section):

$$H_{11} = eI_{xy} (3A_{11} + A_{22} + A_{33}) = 2eI_{xy} A_{11}$$

$$H_{22} = eI_{xy} (A_{11} + 3A_{22} + A_{33}) = 2eI_{xy} A_{22} \quad \text{IV.13}$$

$$H_{33} = eI_{xy} (A_{11} + A_{22} - 3A_{33}) = -2eI_{xy} (A_{11} + A_{22}) .$$

These are also the eigenvalues. The splittings are

$$H_{11} - H_{22} = 2eI_{xy} (A_{11} - A_{22})$$

IV.14

$$H_{22} - H_{33} = 2eI_{xy} (A_{22} - A_{33}) = 2eI_{xy} (A_{11} + 2A_{22}) .$$

As expected, in this model all the orbital degeneracy is lifted.

#### 4. T Model, Expanded Hamiltonian Molecular Orbital Approximation.

This case is of more interest than the previous one, because the spatial degeneracy of the 2p state is completely removed and one has 2 parameters which can be compared in the two theories. Here again  $H_{ij} = 0$ ;  $i \neq j$ . Before we present the eigenvalues of this problem, the following notation is adopted:

$$A'_{11} = e \sum_k (\psi_{BC} | \alpha_{kk}^{11} Q_{kk} | \psi_{BC}) + \alpha_1^{11} (\psi_{BC} | P_x^- | \psi_{BC})$$

$$A'_{22} = e \sum_k (\psi_{BC} | \alpha_{kk}^{22} Q_{kk} | \psi_{BC}) + \alpha_1^{22} (\psi_{BC} | P_x^- | \psi_{BC})$$

IV.15

$$A'_{33} = e \sum_k (\psi_{BC} | \alpha_{kk}^{33} Q_{kk} | \psi_{BC}) + \alpha_1^{33} (\psi_{BC} | P_x^- | \psi_{BC}) .$$

(Note that the integral  $(\psi_{BC} | P_x^- | \psi_{BC}) = \text{constant}$ . See Section III.3a.)

The three eigenvalues are as follows (cf. sect. III.3a, 4a, and IV.1):

$$H_{11} = E_H + E_M + N_x^2 I_{xy} e [3A'_{11} + A'_{22} + A'_{33}] - \frac{1}{2} N_x^2 H'_{11}$$

$$H_{22} = E_H + E_M + N_y^2 I_{xy} e [A'_{11} + 3A'_{22} + A'_{33}] - \frac{1}{2} N_y^2 H'_{22}$$

IV.16

$$H_{33} = E_H + E_M + N_z^2 I_{xy} e [A'_{11} + A'_{22} + 3A'_{33}] - \frac{1}{2} N_z^2 H'_{33} .$$

$$N_x^2 = N_z^2 = 1, \text{ while } N_y^2 = [1 - (2p_y | \psi_{BC})^2]^{-1} = 1 + \frac{a_{22}^2}{1 - a_{22}^2} \text{ (cf. App. D).}$$

$N_x^2 = 1$ , because  $(2p_x | \psi_{BC}) = 0$  in the T model case. The same argument applies to  $N_z^2$ . The level splittings are:

$$H_{11} - H_{22} = 2I_{xy} e (A'_{11} - A'_{22}) - \left( \frac{a_{22}^2}{1 - a_{22}^2} \right) I_{xy} e [A'_{11} + 3A'_{22} + A'_{33}] - \frac{1}{2} (H'_{11} - H'_{22} N_y^2)$$

IV.17

$$H_{22} - H_{33} = 2I_{xy} e (A'_{22} - A'_{33}) + \left( \frac{a_{22}^2}{1 - a_{22}^2} \right) I_{xy} e [A'_{11} + 3A'_{22} + A'_{33}] - \frac{1}{2} (N_y^2 H'_{22} - H'_{33}).$$

Here as in the case of the linear model, there are 3 important terms. The first one is clearly analogous to the crystal field theory result  $2eI_{xy} (A_{ii} - A_{jj})$ . The analogy is even closer here than in the linear case. For instance, the  $A'_{ii}$  (cf. Equation IV.15) are directly related to the quadrupole moment of the molecule (except for a constant). The second term appearing in these level splittings, although dependent on the parameters  $A'_{ii}$ , has a factor  $\frac{(a_{22})^2}{1 - (a_{22})^2}$  which is strongly dependent on the overlap between the charge distributions of the molecule and the atom. The magnitude of this contribution is quite appreciable for  $r_{AB} = 2.5 \text{ \AA}$  (cf. Section IV.2). This term has, of course, no analogue in the crystal field approximation. The third term (cf. Section III.4.a) depends in a very complicated manner on the multicenter integrals, and does not contain any parameters similar to the ones encountered in the crystal field approximation.

## CHAPTER V. DISCUSSION.

The nature of the crystal field approximation has been investigated by studying a complex consisting of a hydrogen atom in the 2p state, and an  $H_2$  molecule in its ground state. This system exhibits the chief phenomenon discussed by crystal field theory, namely the removal of orbital degeneracy. In the investigation, this removal of orbital degeneracy was calculated with ordinary crystal field theory, and with a molecular orbital theory having special features, and the two results compared. These special features are the following: 1.) All terms in the interaction part of the Hamiltonian are expanded in a certain way, which is appropriate for non-overlapping charge distributions. The expansion has the important consequence that the two-particle terms in the Hamiltonian are transformed to sums of products of one-particle Hamiltonians. 2.) The wave functions used to build up the MO's for the whole system are products of eigenfunctions of the separated atom and molecule. Therefore the parts of the Hamiltonian referring to the free atom and molecule are treated easily. 3.) The wave functions for the whole complex are properly antisymmetric under the exchange of any two electrons.

The theory using the special features enumerated above allows one to display the interaction as a sum of two types of terms. (Equation III.3 and III.9). The first type of term is essentially a classical type of term, involving only the charge distribution of the

molecule and the multipole moments of the atom. This type of term is exactly analogous to the usual crystal field approximation. The second type of term involves the overlap of the atom and molecule wave functions and the three center integrals explicitly. In a certain sense this is a correction term to the crystal field approximation. It arises from overlap and the fact that the total wave function of the system is properly antisymmetrized. It is, therefore, clear that the chief formal shortcoming of the crystal field approximation is this neglect of the Pauli exclusion principle.

The same conclusion has been arrived at by Tanabe and Sugano<sup>12</sup> and by Phillips<sup>20</sup>.

It is interesting to point out that a method of approximating the interactions in the many-electron problem analogous to ours has been used successfully by Pluvinaige<sup>21</sup> and by Walsh and Borowitz<sup>22</sup>.

With the general result in hand, the comparison between the crystal field approximation and the EH-SA-MO approximation was worked out in full detail for two special geometries. These are the linear model, with the atomic nucleus on the molecular axis, and the T model, with the atom nucleus on the bisectrix of the molecular axis. In both cases the splittings involved in the lifting of the orbital degeneracy, as obtained in the EH-SA-MO approximation, have three types of terms (Equation IV.10 and IV.17). The first term is again the classical term, and is analogous to the crystal field splitting, though somewhat different in detail. The second term

involves the same parameters as the first term (i.e. those analogous to the crystal field parameters), but also involves the overlap between the atom and molecule functions. The last term involves the three-center integrals introduced by the Pauli exclusion principle, as well as the overlap.

In this analysis it is, therefore, possible to see in some detail the "corrections" to crystal field theory which are needed to take into account overlap and exchange. Unfortunately the present formulation of these corrections is tied very much to the particular system studied, and has therefore the status of a special case, rather than a general formulation. It is to be hoped, however, that this special case is sufficiently clear to indicate the general situation.

The theory presented here seems applicable to one other type of situation than the one contemplated here. This is the so-called strong field case in crystal field theory, where the crystal field is assumed to be so strong as to uncouple the electrostatic repulsions of the electrons in the reference ion. Each electron in the reference ion is then assumed to move independently in the crystal field, and its orbital degeneracy is lifted. The mechanism of this lifting of degeneracy is entirely analogous to the case treated here.

Several tasks remain unfinished. The results of the method should be generalized, the method should be applied to other systems of interest, and the method should be tested by numerical computation.

## APPENDIX A

Expansion of

$$(1 + x + y^2)^{-1/2} = \frac{1}{\sqrt{1 + x + y^2}} = \frac{1}{\sqrt{1 + z}}$$

$$= \frac{1}{\sqrt{1}} + \frac{\frac{1}{2} \binom{1}{1}}{1!} z + \frac{\frac{1}{2} \binom{1}{1}}{2!} z^2 + \frac{\frac{1}{2} \binom{1}{1}}{3!} z^3 + \frac{\frac{1}{2} \binom{1}{1}}{4!} z^4 + \dots$$

Collecting terms of the same order together, we obtain:

|                   |   |
|-------------------|---|
| Zeroth order term | 1   |
| 1st order term    | $-\frac{1}{2} x$  |
| 2nd order term    | $-\frac{1}{2} y^2 + \frac{3}{8} x^2$                                    |
| 3rd order term    | $\frac{3}{4} xy^2 - \frac{15}{3! \cdot 8} x^3$                          |
| 4th order term    | $\frac{3}{8} y^4 - \frac{15}{16} x^2 y^2 + \frac{105}{16 \cdot 4!} x^4$ |

## APPENDIX B

THE EXPANSION OF  $H_{INT}(1;2,3)$  FOR  $r_{1A} + r_{2B} < r_{AB}$ ,  $r_{1A} + r_{3C} < r_{AC}$ . REGION I.

TABLE B.1

LINEAR TERMS IN THE SECOND ORDER PART OF THE EXPANSION

$$\begin{aligned}
 & [x_{2B} r_{AB}^{-3} + x_{3C} r_{AC}^{-3} - 3\alpha v_{2B} r_{AB}^{-1} - 3\gamma u_{3C} r_{AC}^{-1}] x_{1A} \\
 & + [y_{2B} r_{AB}^{-3} + y_{3C} r_{AC}^{-3} - 3\beta v_{2B} r_{AB}^{-1} - 3\delta u_{3C} r_{AC}^{-1}] y_{1A} \\
 & + [z_{2B} r_{AB}^{-3} + z_{3C} r_{AC}^{-3}] z_{1A}
 \end{aligned}$$

TABLE B.2

LINEAR TERMS IN  $x_{1A}$  OF THE THIRD ORDER EXPANSION

$$x_{1A} \left[ \frac{3}{2} \left\{ r_{AB}^{-3} (\alpha r_{2B}^2 + 2V_{2B} x_{2B}) + r_{AC}^{-3} (\gamma r_{3C}^2 + 2U_{3C} x_{3C}) \right\} - \frac{15}{2} (r_{AB}^{-1} \alpha V_{2B}^2 + r_{AC}^{-1} \gamma U_{3C}) \right]$$

$$y_{1A} \left[ \frac{3}{2} \left\{ r_{AB}^{-3} (\beta r_{2B}^2 + 2V_{2B} y_{2B}) + r_{AC}^{-3} (\delta r_{3C}^2 + 2U_{3C} y_{3C}) \right\} - \frac{15}{2} (r_{AB}^{-1} \beta V_{2B}^2 + r_{AC}^{-1} \delta U_{3C}) \right]$$

$$z_{1A} \left[ 3(V_{2B} z_{2B} r_{AB}^{-3} + U_{3C} z_{3C} r_{AC}^{-3}) \right]$$

QUADRATIC TERMS IN  $x_{1A}$  OF THIRD ORDER TERMS

$$\begin{aligned}
& \left[ -\frac{3}{2} \left\{ r_{AB}^{-3}(v_{2B} + 2\alpha x_{2B}) + r_{AC}^{-3}(u_{3C} + 2\gamma x_{3C}) \right\} + 15/2 \left\{ r_{AB}^{-1}\alpha^2 v_{2B} + r_{AC}^{-1}\gamma^2 u_{3C} \right\} \right] x_{1A}^2 \\
& + \left[ -\frac{3}{2} \left\{ r_{AB}^{-3}(v_{2B} + 2\beta y_{2B}) + r_{AC}^{-3}(u_{3C} + 2\delta y_{3C}) \right\} + 15/2 \left\{ r_{AB}^{-1}\beta^2 v_{2B} + r_{AC}^{-1}\delta^2 u_{3C} \right\} \right] y_{1A}^2 \\
& + \left[ -\frac{3}{2} \left( r_{AB}^{-3}v_{2B} + r_{AC}^{-3}u_{3C} \right) \right] z_{1A}^2 \\
& + \left[ -3 \left\{ r_{AB}^{-3}(\alpha y_{2B} + \beta x_{2B}) + r_{AC}^{-3}(\gamma y_{3C} + \delta x_{3C}) \right\} + 15 \left\{ r_{AB}^{-1}v_{2B}\alpha\beta + r_{AC}^{-1}u_{3C}\gamma\delta \right\} \right] x_{1A}y_{1A} \\
& -3 \left\{ r_{AB}^{-3}(\alpha z_{2B}) + r_{AC}^{-3}(\gamma z_{3C}) \right\} x_{1A}z_{1A} \\
& -3 \left\{ r_{AB}^{-3}(\beta z_{2B}) + r_{AC}^{-3}(\delta z_{3C}) \right\} y_{1A}z_{1A}
\end{aligned}$$

LINEAR TERMS IN  $x_{1A}$  FROM THE FOURTH ORDER TERMS

$$\begin{aligned}
 & \left[ -\frac{3}{2} \left\{ r_{AB}^{-5} x_{2B} r_{2B}^2 + r_{AC}^{-5} x_{3C} r_{3C}^2 \right\} + \frac{15}{2} \left\{ r_{AB}^{-3} v_{2B} (x_{2B} v_{2B} + \alpha r_{2B}^2) + r_{AC}^{-3} u_{3C} (x_{3C} u_{3C} + \gamma r_{3C}^2) \right\} - \frac{35}{2} \left\{ r_{AC}^{-1} \gamma u_{3C}^3 + r_{AB}^{-1} \alpha v_{2B}^3 \right\} \right] x_{1A} \\
 & + \left[ -\frac{3}{2} \left\{ r_{AB}^{-5} y_{2B} r_{2B}^2 + r_{AC}^{-5} y_{3C} r_{3C}^2 \right\} + \frac{15}{2} \left\{ r_{AB}^{-3} v_{2B} (y_{2B} v_{2B} + r_{2B}^2 \beta) + r_{AC}^{-3} u_{3C} (y_{3C} u_{3C} + \delta r_{3C}^2) \right\} - \frac{35}{2} \left\{ r_{AB}^{-1} v_{2B}^3 + r_{AC}^{-1} \delta u_{3C}^3 \right\} \right] y_{1A} \\
 & + \left[ -\frac{3}{2} \left\{ r_{AB}^{-5} z_{2B} r_{2B}^2 + r_{AC}^{-5} z_{3C} r_{3C}^2 \right\} + \frac{15}{2} \left\{ r_{AB}^{-3} v_{2B}^2 + r_{AC}^{-3} z_{3C} u_{3C}^2 \right\} \right] z_{1A}
 \end{aligned}$$

TABLE B.5

## QUADRATIC TERMS OF FOURTH ORDER TERMS

$$x_{1A}^2 \left[ \frac{3}{4} \left\{ r_{AB}^{-5} (2x_{2B}^2 + r_{2B}^2) + r_{AC}^{-5} (2x_{3C}^2 + r_{3C}^2) \right\} - \frac{15}{4} \left\{ r_{AB}^{-3} (4\alpha x_{2B} v_{2B} + v_{2B}^2 + \alpha^2 r_{2B}^2) \right. \right.$$

$$\left. + r_{AC}^{-3} (4\gamma x_{3C} u_{3C} + u_{3C}^2 + \gamma^2 r_{3C}^2) \right\} + \frac{105}{4} \left\{ r_{AB}^{-1} \alpha^2 v_{2B}^2 + r_{AC}^{-1} \gamma^2 u_{3C}^2 \right\}$$

$$y_{1A}^2 \left[ \frac{3}{4} \left\{ r_{AB}^{-5} (2y_{2B}^2 + r_{2B}^2) + r_{AC}^{-5} (2y_{3C}^2 + r_{3C}^2) \right\} - \frac{15}{4} \left\{ r_{AB}^{-3} (4\beta y_{2B} v_{2B} + v_{2B}^2 + \beta^2 r_{2B}^2) + r_{AC}^{-3} (4\delta y_{3C} u_{3C} + u_{3C}^2 + \delta^2 r_{3C}^2) \right\} \right.$$

$$\left. + \frac{105}{4} \left\{ r_{AB}^{-1} \beta^2 v_{2B}^2 + r_{AC}^{-1} \delta^2 u_{3C}^2 \right\} \right]$$

$$z_{1A}^2 \left[ \frac{3}{4} \left\{ r_{AB}^{-5} (2z_{2B}^2 + r_{2B}^2) + r_{AC}^{-5} (2z_{3C}^2 + r_{3C}^2) \right\} - \frac{15}{4} \left\{ r_{AB}^{-3} v_{2B}^2 + r_{AC}^{-3} u_{3C}^2 \right\} \right]$$

$$x_{1A} y_{1A} \left[ 3 \left\{ r_{AB}^{-5} x_{2B} y_{2B} + r_{AC}^{-5} x_{3C} y_{3C} \right\} - \frac{15}{2} \left\{ r_{AB}^{-3} (2\beta x_{2B} v_{2B} + 2\alpha\gamma v_{2B} v_{2B} + \alpha\beta r_{2B}^2) + r_{AC}^{-3} (2\delta x_{3C} u_{3C} + 2\gamma\delta u_{3C} u_{3C} + \gamma\delta r_{3C}^2) \right\} \right.$$

$$\left. + \frac{105}{2} \left\{ r_{AB}^{-1} \alpha\beta v_{2B}^2 + r_{AC}^{-1} \gamma\delta u_{3C}^2 \right\} \right]$$

$$x_{1A} z_{1A} \left[ 3 \left\{ r_{AB}^{-5} x_{2B} z_{2B} + r_{AC}^{-5} x_{3C} z_{3C} \right\} - 15 \left\{ r_{AB}^{-3} v_{2B} \alpha z_{2B} + r_{AC}^{-3} u_{3C} \gamma z_{3C} \right\} \right]$$

$$y_{1A} z_{1A} \left[ 3 \left\{ r_{AB}^{-5} y_{2B} z_{2B} + r_{AC}^{-5} y_{3C} z_{3C} \right\} - 15 \left\{ r_{AB}^{-3} v_{2B} \beta z_{2B} + r_{AC}^{-3} u_{3C} \delta z_{3C} \right\} \right]$$

## CUBIC PART OF FOURTH ORDER TERMS

$$\begin{aligned}
& \left[ -3/2 \left\{ r_{AB}^5 x_{2B} + r_{AC}^5 x_{3C} \right\} + 15/2 \left\{ r_{AB}^{-3} (\alpha^2 x_{2B} + \alpha v_{2B}) + r_{AC}^{-3} (\gamma^2 x_{3C} + \gamma u_{3C}) \right\} - 35/2 \left\{ r_{AB}^{-1} \alpha^3 v_{2B} + r_{AC}^{-1} \gamma^3 u_{3C} \right\} \right] x_{1A}^3 \\
+ & \left[ -3/2 \left\{ r_{AB}^5 y_{2B} + r_{AC}^5 y_{3C} \right\} + 15/2 \left\{ r_{AB}^{-3} (\beta^2 y_{2B} + \beta v_{2B}) + r_{AC}^{-3} (\delta^2 y_{3C} + \delta u_{3C}) \right\} - 35/2 \left\{ r_{AB}^{-1} \beta^3 v_{2B} + r_{AC}^{-1} \delta^3 u_{3C} \right\} \right] y_{1A}^3 \\
+ & -3/2 \left\{ r_{AB}^5 z_{2B} + r_{AC}^5 z_{3C} \right\} z_{1A}^3 \\
+ & \left[ -3/2 \left( r_{AB}^5 y_{2B} + r_{AC}^5 y_{3C} \right) + 15/2 \left\{ (\alpha^2 y_{2B} + 2\alpha\beta x_{2B} + \beta v_{2B}) r_{AB}^{-3} + r_{AC}^{-3} (\gamma^2 y_{3C} + 2\gamma\delta x_{3C} + \delta u_{3C}) \right\} \right. \\
& \quad \left. - 35/2 \left\{ r_{AB}^{-1} (\beta\alpha\beta) v_{2B} + r_{AC}^{-1} \delta^3 \gamma^2 u_{3C} \right\} \right] x_{1A}^2 y_{1A} \\
+ & \left[ -3/2 \left( r_{AB}^5 z_{2B} + r_{AC}^5 z_{3C} \right) + 15/2 \left\{ r_{AB}^{-3} (\alpha^2) \cdot z_{2B} + r_{AC}^{-3} \gamma^2 z_{3C} \right\} \right] x_{1A}^2 z_{1A} \\
+ & \left[ -3/2 \left( r_{AB}^5 x_{2B} + r_{AC}^5 x_{3C} \right) + 15/2 \left\{ (\beta^2 x_{2B} + 2\alpha\beta y_{2B} + \alpha v_{2B}) r_{AB}^{-3} + r_{AC}^{-3} (\delta^2 x_{3C} + 2\gamma\delta y_{3C} + \gamma u_{3C}) \right\} \right. \\
& \quad \left. - 35/2 \left\{ r_{AB}^{-1} \beta^2 \alpha v_{2B} + r_{AC}^{-1} \delta^2 \gamma u_{3C} \right\} \right] y_{1A}^2 x_{1A} \\
+ & \left[ -3/2 \left( r_{AB}^5 z_{2B} + r_{AC}^5 z_{3C} \right) + 15/2 \left\{ r_{AB}^{-3} \beta^2 z_{2B} + r_{AC}^{-3} \delta^2 z_{3C} \right\} \right] y_{1A}^2 z_{1A}
\end{aligned}$$

TABLE B.6 (cont.)

$$\begin{aligned}
 & \left[ -\frac{3}{2} (\Gamma_{AB}^{-5} \alpha_{2B} + \Gamma_{AC}^{-5} \alpha_{3C}) + \frac{15}{2} \left\{ \Gamma_{AB}^{-3} \nu_{2B} \alpha + \Gamma_{AC}^{-3} \nu_{3C} \gamma \right\} \right] x_{1A} z_{1A} \\
 & \left[ -\frac{3}{2} (\Gamma_{AB}^{-5} \nu_{2B} + \Gamma_{AC}^{-5} \nu_{3C}) + \frac{15}{2} \left\{ \Gamma_{AB}^{-3} \nu_{2B} \beta + \Gamma_{AC}^{-3} \nu_{3C} \delta \right\} \right] y_{1A} z_{1A} \\
 & + 15 \left\{ \Gamma_{AB}^{-3} \alpha \beta z_{2B} + \Gamma_{AC}^{-3} \gamma \delta z_{3C} \right\} x_{1A} y_{1A} z_{1A}
 \end{aligned}$$

TABLE B.7

FULL EXPANSION FOR THE T-MODEL\*.

2ND ORDER TERMS

$$r_{AB}^{-5} \left[ (y_{AB}^2 - 2x_{AB}^2)P_x - 3x_{AB}y_{AB}P_y \right] x_{1A} + r_{AB}^{-5} \left[ (x_{AB}^2 - 2y_{AB}^2)P_y - 3y_{AB}x_{AB}P_x \right] y_{1A} + r_{AB}^{-5} P_z^2 z_{1A}$$

3RD ORDER TERMS

$$\left\{ 3/2 r_{AB}^{-5} \left[ (3Q_{xx}^- + Q_{yy}^- + Q_{zz}^-)x_{AB} + 2y_{AB}Q_{xy} \right] - 15/2 r_{AB}^{-7} x_{AB} \left[ x_{AB}^2 Q_{xx}^- + 2x_{AB}y_{AB}Q_{xy} + y_{AB}^2 Q_{yy}^- \right] \right\} x_{1A}$$

$$\left\{ 3/2 r_{AB}^{-5} \left[ (3Q_{yy}^- + Q_{xx}^- + Q_{zz}^-)y_{AB} + 2x_{AB}Q_{xy}^- \right] - 15/2 r_{AB}^{-7} y_{AB} \left[ y_{AB}^2 Q_{yy}^- + 2x_{AB}y_{AB}Q_{xy}^- + x_{AB}^2 Q_{xx}^- \right] \right\} y_{1A}$$

$$3r_{AB}^{-5} \left[ x_{AB}Q_{zx}^- + y_{AB}Q_{zy}^- \right] z_{1A}$$

$$+ \left\{ 3/2 r_{AB}^{-5} \left[ 3x_{AB}P_x^- + y_{AB}P_y^- \right] + 15/2 r_{AB}^{-7} x_{AB}^2 \left[ x_{AB}P_x^- + y_{AB}P_y^- \right] \right\} x_{1A}^2$$

$$\left\{ -3/2 r_{AB}^{-5} \left[ 3y_{AB}P_y^- + x_{AB}P_x^- \right] + 15/2 r_{AB}^{-7} y_{AB}^2 \left[ y_{AB}P_y^- + x_{AB}P_x^- \right] \right\} y_{1A} - 3/2 r_{AB}^{-5} \left[ x_{AB}P_x^- + y_{AB}P_y^- \right] z_{1A}^2$$

$$\left\{ -3r_{AB}^{-5} \left[ x_{AB}P_y^- + y_{AB}P_x^- \right] + 15r_{AB}^{-7} x_{AB}y_{AB} \left[ x_{AB}P_x^- + y_{AB}P_y^- \right] \right\} x_{1A}y_{1A} - 3r_{AB}^{-5} x_{AB}P_z^2 z_{1A} - 3r_{AB}^{-5} y_{AB}P_z^2 z_{1A}$$

\*To obtain the desired cartesian form for  $H_{INT}(1;2,3)$  for the linear model:

Replace everywhere  $f(x_{AB}, y_{AB})P_x^{\pm}$ , by  $f(x_{AB}, 0)x_B \pm f(x_{AC}, 0)x_C$ . Similar rules hold for  $Q_{ij}^{\pm}$ ,  $r_{klm}^{\pm}$ .

TABLE B.7 (cont.)

4TH ORDER TERMS

$$\begin{aligned}
 & \left\{ \begin{aligned}
 & - 3/2 r_{AB}^{-5} [T_{xxx} + T_{xyy} + T_{zzz}] + 15/2 r_{AB}^{-7} (2T_{xxx} + T_{xyy} + T_{zzz}) + x_{AB} y_{AB} (3T_{xxy}^{-} + T_{yzz}^{-} + T_{xyy}^{-}) + y_{AB}^2 T_{xyy} \\
 & - 35/2 r_{AB}^{-9} x_{AB}^3 [x_{AB}^3 T_{xxx} + 3x_{AB}^2 y_{AB} T_{xxy} + 3x_{AB} y_{AB}^2 T_{xyy} + y_{AB}^3 T_{yyy}]
 \end{aligned} \right\} x_{1A} \\
 & + \left\{ \begin{aligned}
 & - 3/2 r_{AB}^{-5} [T_{yyy} + T_{xxy} + T_{yzz}] + 15/2 r_{AB}^{-7} [x_{AB}^2 T_{xxy} + x_{AB} y_{AB} (3T_{xxy}^{-} + T_{xzz}^{-} + T_{xyy}^{-}) + y_{AB}^2 (2T_{yyy} + T_{xxy} + T_{yzz})] \\
 & - 35/2 r_{AB}^{-9} [y_{AB}^3 T_{yyy} + 3y_{AB}^2 x_{AB} T_{xxy} + 3y_{AB} x_{AB}^2 T_{xyy} + x_{AB}^3 T_{xxx}]
 \end{aligned} \right\} y_{1A} \\
 & + \left[ - 3/2 r_{AB}^{-5} (T_{zzz} + T_{xxx} + T_{zyy}) + 15/2 r_{AB}^{-7} (x_{AB}^2 T_{zzx} + 2x_{AB} y_{AB} T_{zxy} + y_{AB}^2 T_{zyy}) \right] z_{1A} \\
 & + \left\{ \begin{aligned}
 & 3/4 r_{AB}^{-5} (3Q_{xx} + Q_{yy} + Q_{zz}) - 15/4 r_{AB}^{-7} (6x_{AB}^2 Q_{xx} + y_{AB}^2 Q_{yy} + x_{AB}^2 Q_{yy} + x_{AB}^2 Q_{zz}) \\
 & + (105/4) r_{AB}^{-9} [x_{AB}^2 Q_{xx} + 2x_{AB} y_{AB} Q_{xy} + (y_{AB}^2) (Q_{yy})]
 \end{aligned} \right\} x_{1A}^2 \\
 & + \left\{ \begin{aligned}
 & 3/4 r_{AB}^{-5} (3Q_{yy} + Q_{xx} + Q_{zz}) - 15/4 r_{AB}^{-7} (6y_{AB}^2 Q_{yy} + x_{AB}^2 Q_{xx} + y_{AB}^2 Q_{xx} + y_{AB}^2 Q_{zz}) \\
 & + 105/4 r_{AB}^{-9} [y_{AB}^2 Q_{yy} + 2x_{AB} y_{AB} Q_{xy} + x_{AB}^2 Q_{xx}]
 \end{aligned} \right\} y_{1A}^2 \\
 & + \left[ 3/4 r_{AB}^{-5} (3Q_{zz} + Q_{xx} + Q_{yy}) - 15/4 r_{AB}^{-7} [x_{AB}^2 Q_{xx} + 2x_{AB} y_{AB} Q_{xy} + y_{AB}^2 Q_{yy}] \right] z_{1A}^2 \\
 & + \left\{ \begin{aligned}
 & 3 z_{A0}^{-5} Q_{xy} - \frac{15}{2} z_{A0}^{-7} [3 x_{AE} y_{AB} (Q_{xx} + Q_{yy}) + 2(x_{AB}^2 + y_{AB}^2) Q_{xy}] Q_{xy} + x_{AB} y_{AB} [x_{AB}^2 Q_{xx} + y_{AB}^2 Q_{yy} + 2x_{AB} y_{AB} Q_{xy}] \\
 & 105/2 z_{A0}^{-9} x_{AB} y_{AB} [x_{AB}^2 Q_{xx} + y_{AB}^2 Q_{yy} + 2x_{AB} y_{AB} Q_{xy}]
 \end{aligned} \right\} x_{1A} y_{1A}
 \end{aligned}$$

TABLE B.7 (cont.)

$$\begin{aligned}
& \left[ 3r_{AB}^5 Q_{xz} - 15r_{AB}^7 x_{AB}^0 x_{zz} + y_{AB}^0 y_{zz} \right] x_{1A}^2 z_{1A} + \left[ 3r_{AB}^5 Q_{yz} - 15r_{AB}^7 y_{AB}^0 (x_{AB}^0 x_{zz} + y_{AB}^0 y_{zz}) \right] y_{1A}^2 z_{1A} \\
& + \left[ -3/2 r_{AB}^5 P_x + (15/2) r_{AB}^7 (x_{AB}^0) (2P_x^{x_{AB}} + y_{AB}^0 P_x^y) - 35/2 r_{AB}^9 x_{AB}^3 (x_{AB}^0 P_x + y_{AB}^0 P_x^y) \right] x_{1A}^3 \\
& + \left[ -(3/2) r_{AB}^5 P_y + (15/2) r_{AB}^7 (y_{AB}^0) (2y_{AB}^0 P_y + x_{AB}^0 P_x^y) - (35/2) r_{AB}^9 y_{AB}^3 (y_{AB}^0 P_y + x_{AB}^0 P_x^y) \right] y_{1A}^3 - 3/2 r_{AB}^5 P_z^2 z_{1A} \\
& + \left[ -3r_{AB}^5 P_x + (15/2) r_{AB}^7 \left[ (x_{AB}^2 + y_{AB}^2) P_x + 3x_{AB}^y y_{AB}^0 P_x^y \right] - 35/2 (3x_{AB}^2 y_{AB}^0) r_{AB}^9 (x_{AB}^0 P_x^y + y_{AB}^0 P_x^y) \right] x_{1A}^2 y_{1A} \\
& + \left[ -3r_{AB}^5 P_y + 15/2 r_{AB}^7 \left[ (y_{AB}^2 + x_{AB}^2) P_y + 3x_{AB}^y y_{AB}^0 P_y^y \right] - 35/2 (3x_{AB}^2 y_{AB}^0) r_{AB}^9 (y_{AB}^0 P_y^y + x_{AB}^0 P_x^y) \right] y_{1A}^2 x_{1A} \\
& + \left[ -3/2 r_{AB}^5 + 15/2 r_{AB}^7 x_{AB}^2 \right] P_z^2 x_{1A}^2 + \left[ -(3/2) r_{AB}^5 + 15/2 r_{AB}^7 y_{AB}^2 \right] P_z^2 y_{1A}^2 + \left[ 3/2 r_{AB}^5 P_x + 15/2 r_{AB}^7 x_{AB}^0 (x_{AB}^0 P_x + y_{AB}^0 P_x^y) \right] z_{1A}^2 x_{1A} \\
& + \left[ -3/2 r_{AB}^5 P_y + 15/2 r_{AB}^7 y_{AB}^2 \right] P_z^2 y_{1A}^2 + \left[ 3/2 r_{AB}^5 P_y + 15/2 r_{AB}^7 y_{AB}^0 (x_{AB}^0 P_x^y + y_{AB}^0 P_y^y) \right] z_{1A}^2 y_{1A} \\
& + (15 r_{AB}^7 x_{AB} y_{AB} P_z^2) \quad (x_{1A} y_{1A} z_{1A})
\end{aligned}$$

## APPENDIX C

## THE EXPANSION B + B'

We present the third and fourth order terms in the expansion B + B'.  
The first and second order terms were given in Section II.5.

## 1. THIRD ORDER TERMS (B + B')

$$\begin{aligned}
& 3/2 r_{1A}^{-3} [ r_{2B}^2 W_{AB} + r_{3C}^2 W_{AC} - 2\vec{r}_{2B} \cdot \vec{r}_{AB} W_{AB} - 2\vec{r}_{3C} \cdot \vec{r}_{AC} W_{AC} - (\vec{r}_{AB} - \vec{r}_{2B}) \cdot (\vec{r}_{AB} - \vec{r}_{2B}) W_{2B} \\
& \quad - (\vec{r}_{AC} - \vec{r}_{3C}) \cdot (\vec{r}_{AC} - \vec{r}_{3C}) W_{3C} ] \\
& + (3/2) r_{AB}^{-3} r_{2B}^2 V_{2B} + 3/2 r_{AC}^{-3} r_{3C}^2 U_{3C} \\
& + 5/2 r_{1A}^{-1} [ 3(W_{AB})^2 W_{2B} - 3W_{AB} W_{2B}^2 + W_{2B}^3 + 3W_{AC}^2 W_{3C} - 3W_{AC} W_{3C}^2 + W_{3C}^3 ] \\
& - 5/2 r_{AB}^{-1} V_{2B}^3 - 5/2 r_{AC}^{-1} U_{3C}^3
\end{aligned}$$

## APPENDIX C (continued)

## 2. FOURTH ORDER TERMS (B + B')

$$\begin{aligned}
& 3/8 r_{1A}^{-5} [ r_{2B}^4 + 4(\vec{r}_{AB} \cdot \vec{r}_{2B})^2 - 4(\vec{r}_{AB} \cdot \vec{r}_{2B})(r_{AB}^2 + r_{2B}^2) + 2r_{AB}^2 r_{2B}^2 \\
& \quad + r_{3C}^4 + 4(\vec{r}_{AC} \cdot \vec{r}_{3C})^2 - 4(\vec{r}_{AC} \cdot \vec{r}_{3C})(r_{AC}^2 + r_{3C}^2) + 2r_{AC}^2 r_{3C}^2 ] \\
& - (3/8) r_{AB}^{-5} r_{2B}^4 - 3/8 r_{AC}^{-5} r_{3C}^4 \\
& - 15/4 r_{1A}^{-3} [ (\vec{r}_{AB} - \vec{r}_{2B}) \cdot (\vec{r}_{AB} - \vec{r}_{2B}) (-2W_{AB}W_{2B} + W_{2B}^2) \\
& \quad + (\vec{r}_{AC} - \vec{r}_{3C}) \cdot (\vec{r}_{AC} - \vec{r}_{3C}) (-2W_{AC}W_{3C} + W_{3C}^2) \\
& - (2\vec{r}_{AB} \cdot \vec{r}_{2B} - r_{2B}^2) W_{AB}^2 - (2\vec{r}_{AC} \cdot \vec{r}_{3C} - r_{3C}^2) W_{AC}^2 ] \\
& + (15/4) r_{AB}^{-3} r_{2B}^2 V_{2B}^2 + (15/4) r_{AC}^{-3} r_{3C}^2 U_{3C}^2 \\
& + 35/8 r_{1A}^{-1} [ -4W_{AB}^3 W_{2B} + 6W_{AB}^2 W_{2B}^2 - 4W_{AB} W_{2B}^3 + W_{2B}^4 \\
& \quad - 4W_{AC}^3 W_{3C} + 6W_{AC}^2 W_{3C}^2 - 4W_{AC} W_{3C}^3 + W_{3C}^4 \\
& - (35/8) r_{AB}^{-1} V_{2B}^4 - (35/8) r_{AC}^{-1} U_{3C}^4
\end{aligned}$$

## APPENDIX D

NORMALIZATION CONSTANT  $N_1$ 

The function to be normalized is

$$\begin{aligned} \Phi_i &= [2P_{A,1}(1)\alpha(1)\Psi_M(2,3) + 2P_{A,1}(2)\alpha(2)\Psi_M(3,1) + 2P_{A,1}\alpha(3)\Psi_M(1,2)]^{3^{-1/2}} \\ &= \phi_i(1,2,3). \end{aligned} \quad (D.1)$$

First we show that

$$(\Phi_i(1,2,3) | 2P_{A,1}(1)\alpha(1)\Psi_M(2,3))$$

$$= (\Phi_i(1,2,3) | 2P_{A,1}(2)\alpha(2)\Psi_M(3,1)) \quad (D.2)$$

$$= (\Phi_i(1,2,3) | 2P_{A,1}(3)\alpha(3)\Psi_M(1,2)) \quad (D.3)$$

The proof is as follows. We interchange the labeling of electrons 1 and 2 in Eq. D.2. This leaves the integral invariant.

$$(\Phi_i(1,2,3) | 2P_{A,1}(1)\alpha(1)\Psi_M(2,3)) \equiv (\Phi_i(213) | 2P_{A,1}(2)\alpha(2)\Psi_M(1,3)) \quad (D.4)$$

$$= -(\Phi_i(123) | 2P_{A,1}(2)\alpha(2)\Psi_M(1,3)) = (-1)(-1)(\Phi_i(123) | 2P_{A,1}(2)\alpha(2)\Psi_M(3,1)) \quad (D.5)$$

The proof of eq. D.3 proceeds in the same way as the one for eq. D.2. A consequence of eq. D.2 and D.3 is that

$$(\Phi_i | \Phi_i) = 3^{-1/2} (\Phi_i(123) | 2P_{A,1}(1)\alpha(1)\Psi_M(2,3)) \quad (D.6)$$

$$\text{But } (\Phi_i(123) | 2P_{A,1}(1)\alpha(1)\Psi_M(2,3)) =$$

$$3^{-1/2} \left\{ \begin{aligned} & (2P_{A,1}(1)\alpha(1)\Psi_M(2,3) | 2P_{A,1}(1)\alpha(1)\Psi_M(2,3)) \\ & + (2P_{A,1}(2)\alpha(2)\Psi_M(3,1) | 2P_{A,1}(1)\alpha(1)\Psi_M(2,3)) \\ & + (2P_{A,1}(3)\alpha(3)\Psi_M(1,2) | 2P_{A,1}(1)\alpha(1)\Psi_M(2,3)) \end{aligned} \right\}$$

$$= 3^{-1/2} [1 - (2P_{A,1} | \Psi_{BC})^2] \quad (D.7)$$

## APPENDIX D (cont.)

This last result was obtained by recalling the definition of  $\Psi_M(k,1)$  (Eq. III.1). Using Eq. D.7,  $(\Phi_i | \Phi_i) = [1 - (2P_{A,1} | \Psi_{BC})^2]$

Thus  $N_i = [1 - (2P_{A,1} | \Psi_{BC})^2]^{-1/2}$ , and  $\psi_i = N_i \phi_i$ , where  $(\psi_i | \psi_i) = 1$ .

## APPENDIX E

ORTHONORMALIZATION OF THE  $\psi_1$ 's

From Appendix D we know that  $(\psi_1 | \psi_2) = (\psi_x | \psi_y) = -(2p_x | \psi_{BC})(\psi_{BC} | 2p_y) = -a_{12}$

Also from symmetry consideration  $(2p_z | \psi_{BC}) = 0$ ; thus,  $a_{13} = a_{23} = 0$ .

We use the well known Gram-Schmidt orthonormalization process.

Let  $\Phi_I = \psi_x$ ,

then  $\Phi_{II} = N_{II} (a\psi_x + \psi_y)$

We determine a:

$$(\Phi_I | \Phi_{II}) = 0 = a + (\psi_x | \psi_y). \text{ Thus } a = a_{12}$$

$$(\Phi_{II} | \Phi_{II}) = 1 = N_{II}^2 (1 - a_{12}^2)$$

$$\text{thus } \Phi_{II} = \frac{a_{12}\psi_x + \psi_y}{[1 - a_{12}^2]^{1/2}}$$

Let  $\Phi_{III} = (b\Phi_I + c\Phi_{II} + \psi_z)N_{III}$ . We determine b and c.

Then  $(\Phi_I | \Phi_{III}) = (b - a_{13})N_{III} = 0$ , and since  $a_{13} = 0$ ,  $b = 0$ .

Now  $(\Phi_{II} | \Phi_{III}) = c + (\psi_y | \psi_z) = 0$ . Since  $a_{23} = 0$ ,  $c = 0$ ;

thus,  $\Phi_{III} = \psi_z$

## APPENDIX F

## PROOF OF THE FORM OF THE MATRIX ELEMENT EQ. III.3.

We show explicitly how we arrive at the result III.3. for the diagonal elements  $H_{ii}$ . Then we show how to generalize the result when  $i \neq j$ . We make use of eq. D.6, and the fact <sup>that</sup>  $\Lambda H_T$  is invariant under relabeling the electrons to obtain:

$$(\Psi_i | H_T | \Psi_j) = 3^{1/2} N_j (\Psi_i | H_T | 2p_{A,j}(1)\alpha(1)\Psi_M(2,3)) \quad (F.1)$$

$$= 3^{1/2} N_j (\Psi_i | H_H(1) + H_M(2,3) + H_{INT}(1;2,3) | 2p_{A,j}(1)\alpha(1)\Psi_M(2,3)). \quad (F.2)$$

Making use of the fact that the wave functions  $2p_{A,i}$  and  $\Psi_M$  are eigenstates of  $H_H$  and  $H_M$  respectively, we obtain the following:

$$\begin{aligned} (\Psi_i | H_T | \Psi_j) = & \\ & 3^{1/2} N_j \left[ E_H (\Psi_i | 2p_{A,1}(1)\alpha(1)\Psi_M(2,3)) + E_M (\Psi_i | 2p_{A,1}(1)\alpha(1)\Psi_M(2,3)) \right. \\ & \left. + (\Psi_i | H_{INT}(1;2,3) | 2p_{A,1}(1)\alpha(1)\Psi_M(2,3)) \right] \quad (F.3) \end{aligned}$$

Using the results of eq. F.1, and F.2, F.3 becomes (for  $i = j$ )

$$= E_H + E_M + 3^{1/2} N_1 (\Psi_i | H_{INT}(1;2,3) | 2p_{A,1}(1)\alpha(1)\Psi_M(2,3)) \quad (F.4)$$

$$= E_H + E_M + 3^{1/2} N_1 (\Psi_i | \sum H_A^{kl}(1)(H_B^{lm}(2) + H_C^{lm}(3)) | 2p_{A,1}(1)\alpha(1)\Psi_M(2,3)) \quad F.5$$

(cf. Table III.1). F.5 is correct up to and including  $l$ th order terms in the expansion of  $H_{INT}$ . Recalling the expression for  $\Psi_i$  (Eq. III.1), Eq. F.5 is equal to

## APPENDIX F (cont.)

$$= E_H + E_M + \sum_{k, l, m} N_1^2 \left\{ \begin{array}{l} (2P_{A,1} | H_A^{kl} | 2P_{A,1}) (\Psi_{BC} | H_B^{lm} + H_C^{lm} | \Psi_{BC}) \\ -\frac{1}{2} (\Psi_{BC} | H_A^{kl} | 2P_{A,1}) (2P_{A,1} | H_B^{lm} + H_C^{lm} | \Psi_{BC}) \\ -\frac{1}{2} (2P_{A,1} | \Psi_{BC}) (\Psi_{BC} | H_A^{kl} | 2P_{A,1}) (\Psi_{BC} | H_B^{lm} + H_C^{lm} | \Psi_{BC}) \end{array} \right\} \quad (F.6)$$

Since  $N_1^2 = [1 - (2P_{A,1} | \Psi_{BC})^2]^{-1}$ , we find the result (III.3). The factor  $-\frac{1}{2}$  arises because of the spin dependence of the wave function, and the resulting integration over the spin coordinates. Thus, when evaluating

$$(2P_{A,1}(2) \alpha(2) \Psi_M(3,1) | H_A^{kl}(1) (H_B^{lm}(2) + H_C^{lm}(3)) | 2P_{A,1}(1) \alpha(1) \Psi_M(2,3))$$

we must recall that  $\Psi_M(2,3) = \Psi_{BC}(2) \Psi_{BC}(3) [\alpha(3) \beta(1) - \alpha(1) \beta(3)] j^{-1/2}$ .

Therefore, we must perform the following integration over the spin coordinates :

$$\left( \alpha(2) \left[ \frac{\alpha(3) \beta(1) - \alpha(1) \beta(3)}{\sqrt{2}} \right] | \alpha(1) \left[ \frac{\alpha(2) \beta(3) - \alpha(3) \beta(2)}{\sqrt{2}} \right] \right) = -\frac{1}{2},$$

since the only nonvanishing integral is

$$-\frac{1}{2} (\alpha(2) \alpha(1) \beta(3) | \alpha(1) \alpha(2) \beta(3))$$

The proof for  $H_{ij}$ , for  $i \neq j$  is identical except that one replaces in Eq. F.6

$N_1^2$  by  $N_1 N_j$ ,  $E_H + E_M$  by  $(E_H + E_M) [\delta_{ij} - (2P_{A,1} | \Psi_{BC})(2P_{A,j} | \Psi_{BC})] N_1 N_j$ ,

and the second index  $i$  by  $j$ .

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Figure 1. The system H - H<sub>2</sub>. The nucleus A belongs to the H atom, the nuclei B and C to the H<sub>2</sub> molecule. The coordinate systems used in the calculation are indicated. Thus  $x_{1A}$  is the x-coordinate of electron 1 measured from nucleus A.

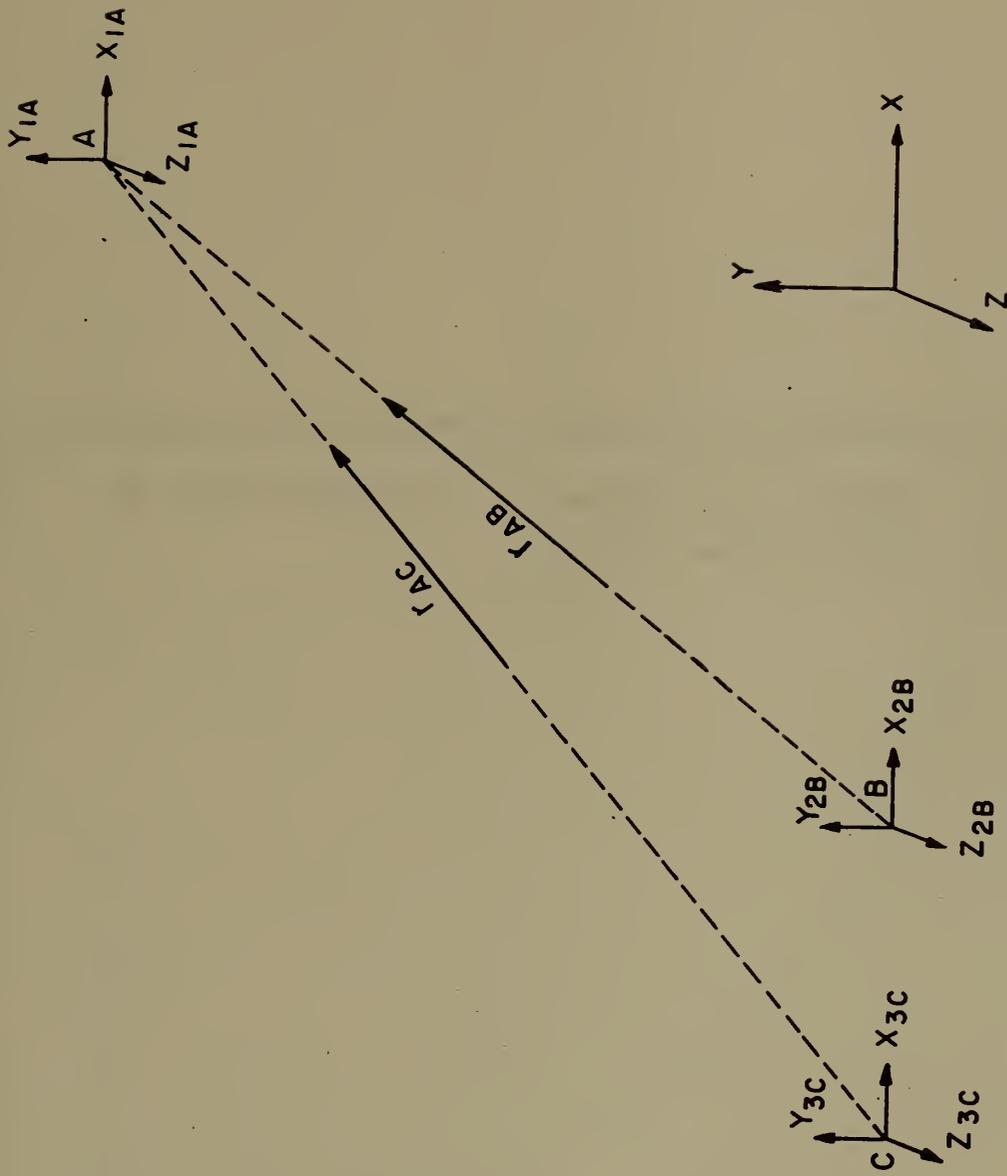


FIG.1 The system H - H<sub>2</sub>

Figure 2. An analysis of the effect of overlap. The scaling factor,  $(2p_x|\psi_{BC})^2 [1 - (2p_x|\psi_{BC})^2]^{-1}$  is plotted against the overlap integral  $(2p_x|\psi_{BC})$ .

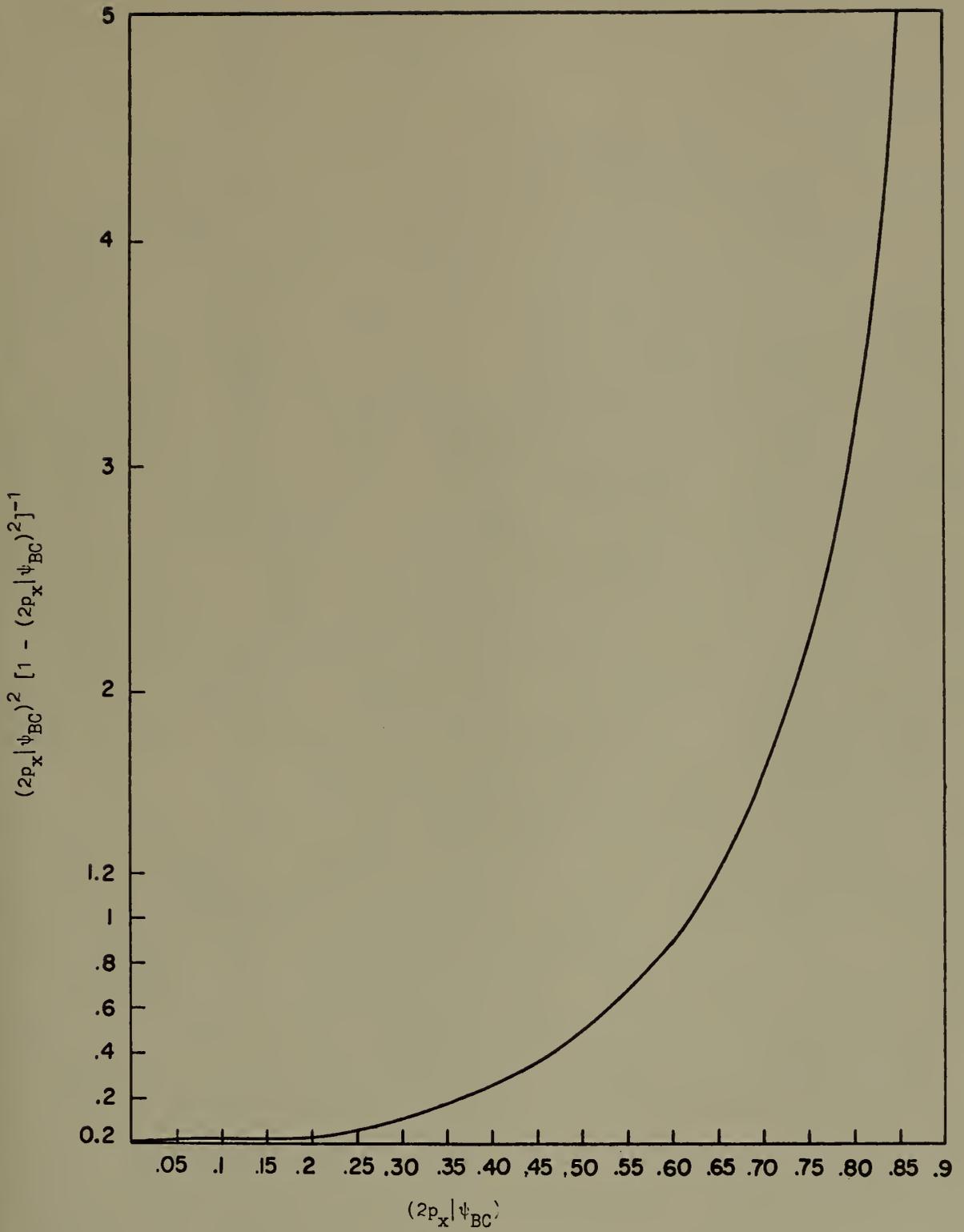


Fig. 2 An analysis of the effect of overlap



U.S. DEPARTMENT OF COMMERCE

Frederick H. Mueller, *Secretary*

NATIONAL BUREAU OF STANDARDS

A. V. Astle, *Director*



THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colo., is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D.C.

**ELECTRICITY.** Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Inductrics.

**METROLOGY.** Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

**HEAT.** Temperature Physics. Heat Measurements. Cryogenic Physics. Rheology. Molecular Kinetics. Free Radicals Research. Equation of State. Statistical Physics. Molecular Spectroscopy.

**RADIATION PHYSICS.** X-Ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

**CHEMISTRY.** Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrochemistry. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

**MECHANICS.** Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Combustion Controls.

**ORGANIC AND FIBROUS MATERIALS.** Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

**METALLURGY.** Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

**MINERAL PRODUCTS.** Engineering Ceramics. Glass. Refractories. Enameled Metals. Constitution and Microstructure.

**BUILDING RESEARCH.** Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials.

**APPLIED MATHEMATICS.** Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

**DATA PROCESSING SYSTEMS.** Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Applications Engineering.

**ATOMIC PHYSICS.** Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics.

**INSTRUMENTATION.** Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

**Office of Weights and Measures.**

BOULDER, COLO.

**CRYOGENIC ENGINEERING.** Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

**IONOSPHERE RESEARCH AND PROPAGATION.** Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services.

**RADIO PROPAGATION ENGINEERING.** Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

**RADIO STANDARDS.** High frequency Electrical Standards. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time Standards. Electronic Calibration Center. Millimeter-Wave Research. Microwave Circuit Standards.

**RADIO SYSTEMS.** High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems. Space Telecommunications.

**UPPER ATMOSPHERE AND SPACE PHYSICS.** Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

